TECHNICAL PROGRESS REVIEWS

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# REACTOR FUEL PROCESSING

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY

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JANUARY 1959 VOLUME 2 NUMBER 1

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# REACTOR FUEL PROCESSING

a review of recent developments prepared by

ARGONNE NATIONAL LABORATORY

JANUARY 1959 VOLUME 2 NUMBER 1

# *foreword*

This quarterly review of *Reactor Fuel Processing* has been prepared at the request of the U. S. Atomic Energy Commission, Division of Information Services. It is the first issue of Volume 2, intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this broad field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Usually these reviews do not include foreign literature. The Geneva Conference, however, is an unusual circumstance, and so in this and the next Review an attempt will be made to cover all the U. S. and foreign papers, both those given orally and those written for the Conference record, which are pertinent to this field.

Interpretation of results, where given, represents the opinions of the editors of the Review who are personnel of the Argonne National Laboratory, Chemical Engineering Division. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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# REACTOR FUEL PROCESSING

## *COMMERCIAL ASPECTS OF FUEL REPROCESSING*

On Oct. 15, 1958, the AEC invited industry and research institutions to submit proposals to provide services and facilities and to perform research and development in any of six major areas of fuel-cycle development[1] as follows:

1. Development of chemical processes related to the total fuel cycle but excluding the obtaining of concentrates from the ore.
2. Development of fuel-element materials and designs suitable for use in power reactors.
3. Irradiation and post-irradiation examination of selected fuel-element materials.
4. Development of fabrication and inspection techniques which lower fuel-element manufacturing costs.
5. Development, fabrication, and testing, including exposures in test reactors, either singly or in small numbers, of prototype fuel elements of a variety of promising types, especially those capable of operating at higher temperatures and higher burn-ups.
6. Selection of proven fuel-element types developed in the program, and fabrication of large numbers of those elements for subsequent use as multi-ton batches in full-scale power reactors.

No limitation has been placed on the design or type of fuel elements to be developed or on the fissionable material to be used in such elements. However, all proposals must be based on the latest technology and must be directed toward making a significant achievement in lowering fuel-cycle costs. Any research and development assistance requested from AEC must include an estimate of cost per fiscal year, starting with Fiscal Year 1959, and a well-defined realistic justification for the work proposed. Similarly, the proposal should include an estimate of the fissionable and fertile materials required.

Commission assistance may include the provision of hot-cell facilities and irradiation space in test reactors and arrangements for obtaining space for operational use in commercial-size power reactors.

It was required that expressions of interest to participate in this program be submitted to the Director, Division of Reactor Development, U. S. Atomic Energy Commission, Washington 25, D. C., by Oct. 29, 1958, and proposals were required by Nov. 28, 1958.

The AEC also announced,[2] on Sept. 26, 1958, that it was prepared to sell high-purity $U^{238}$ (>99.97 per cent $U^{238}$) in three forms:*

| | Dollars/g uranium |
|---|---|
| $U_3O_8$ (uranium oxide) | $15.25 |
| Cast rod (⅛-in. diameter) | 16.50 |
| Metal foil | 16.75 |

In the *Federal Register* of June 28, 1958, the AEC announced that it would sell depleted uranium as uranium hexafluoride at the price schedule shown in Table I-1.

A list of materials and services which are now available from commercial sources and for which the AEC[3] no longer acts as a supplier is shown as follows:

*Materials*

1. Thorium metal and oxides.
2. Natural-uranium metal.
3. Natural-uranium compounds.
4. Heavy water in quantities less than 125 lb (available through commercial retailers).

* Prices do not include transportation or the standard handling charge of $14.00 per shipment.

Table I-1 BASE CHARGES FOR DEPLETED URANIUM FURNISHED BY AEC AS URANIUM HEXAFLUORIDE (FOB PADUCAH, KY.)

| Assay weight fraction $U^{235}$ | Charge, $/kg U |
|---|---|
| 0.0036 and lower | $5.00 |
| 0.0040 | 8.15 |
| 0.0050 | 16.65 |
| 0.0052 | 18.65 |
| 0.0054 | 20.65 |
| 0.0056 | 22.65 |
| 0.0058 | 24.75 |
| 0.0060 | 26.90 |
| 0.0062 | 29.00 |
| 0.0064 | 31.25 |
| 0.0066 | 33.50 |
| 0.0068 | 35.75 |
| 0.0070 | 38.15 |

*Services*

1. Conversion of uranium hexafluoride, enriched or depleted, into uranium metal, oxides, and other enriched or depleted uranium compounds.
2. Recovery of uranium in scrap resulting from uranium conversion, fuel-element fabrication, etc. (The AEC is continuing to furnish the service of recovery of uranium and plutonium in irradiated fuel from nuclear reactors and facilities.)
3. Fabrication of fuel elements.
4. Gamma-irradiation services and experiments.

The AEC also gave notice of its intention to license two New England firms (Walker Trucking Co., New Britain, Conn., and New England Tank Cleaning Co., Cambridge, Mass.) to collect low-level radioactive wastes and to dispose of them at sea[4] and to permit a west coast firm (Nuclear Engineering Co., Inc., Walnut Creek, Calif.) to dispose of larger quantities than under its present license.[5]

At a nuclear fuels transportation meeting in Chicago in July, the AEC indicated that fuel from private nuclear reactors would be processed at one of four sites depending on the type of fuel.[6] All depleted, natural, and slightly enriched uranium fuels (up to 5 per cent $U^{235}$) will be processed at Hanford; all highly-enriched uranium fuels, at Idaho; all thorium-bearing fuels, as well as 20 per cent enriched aluminum-clad uranium fuels as used in a number of overseas research and test reactors, at Oak Ridge. The processing facilities at Savannah River will be used for special type cores such as that planned for the fast reactor at Lagoona Beach.

## *References*

1. AEC Invites Industry to Participate in Fuel Cycle Development Program, AEC Press Release A-269, Oct. 15, 1958.
2. Uranium Enriched to 99.97 Per Cent $U^{235}$ Offered for Sale by AEC, AEC Press Release A-252, Sept. 26, 1958.
3. Materials and Services Available Commercially Are Listed by AEC for Information of Industry, AEC Press Release A-231, Sept. 5, 1958.
4. AEC Proposes to License New England Firms for Disposal of Radioactive Wastes at Sea, AEC Press Release A-223, Aug. 28, 1958.
5. California Firm Could Handle Additional Quantities of Radioactive Wastes Under Proposed AEC License, AEC Press Release A-235, Sept. 8, 1958.
6. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 5, No. 8, August 1958.

There were two accidents reported during the quarter. The first was an explosion in a silver nitrate reactor used to absorb iodine vapors from a (Hanford) dissolver.[1] There were no personal injuries as the effects of the incident were confined to a closed process cell.

This incident followed an attempt to unplug a silver reactor that had been regenerated approximately ten times. An ammonium hydroxide flush was used to unplug the reactor. This was effective in decreasing the flow resistance of the unit. The reactor was then given a thorough water flush, dried, sprayed with silver nitrate solution, and returned to service. Shortly thereafter, a rapid exothermic reaction occurred. Laboratory information has shown that this reaction resulted from the decomposition of an unstable product that has been formed by reaction with ammonia. The particular compound has not been identified, nor has the source of the ammonia been established conclusively.

The second incident, which has received considerable publicity, was the criticality accident at Oak Ridge on June 16, 1958.[2–5] This incident resulted in the exposure of eight employees in amounts ranging from 20 to 320 rad.

On the afternoon of the incident, eight men were working in a wing of a processing plant. A chemical operator noticed a sudden blue flash and immediately thereafter heard the evacuation alarm sound, indicating existence of excessive radiation hazards. He and the others promptly left the building.

Immediate efforts were directed toward determining whether any individual had been exposed to excessive radiation, providing medical care, and in decontaminating and cleaning up the affected building wing. By this time it had been established that a criticality or nuclear excursion had occurred in a 55-gal stainless-steel drum.

A diagram showing the principal equipment involved in the accident is shown in Fig. 1. Immediately prior to the accident, tanks No. 3 and 4 were being leak-tested with water. Before this, and unknown to the operator, probably due to valve leakage and/or operator error, enriched uranium solution had flowed from storage tank No. 1 partially filling tank No. 2 and the piping connecting the three tanks.

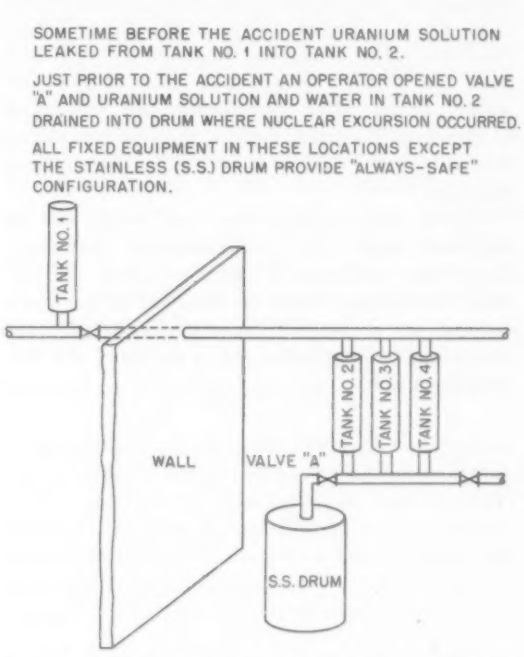
SOMETIME BEFORE THE ACCIDENT URANIUM SOLUTION LEAKED FROM TANK NO. 1 INTO TANK NO. 2.
JUST PRIOR TO THE ACCIDENT AN OPERATOR OPENED VALVE "A" AND URANIUM SOLUTION AND WATER IN TANK NO. 2 DRAINED INTO DRUM WHERE NUCLEAR EXCURSION OCCURRED.
ALL FIXED EQUIPMENT IN THESE LOCATIONS EXCEPT THE STAINLESS (S.S.) DRUM PROVIDE "ALWAYS-SAFE" CONFIGURATION.
TANK NO. 1
TANK NO. 2
TANK NO. 3
TANK NO. 4
WALL
VALVE "A"
S.S. DRUM

Fig. 1—Schematic diagram of equipment involved in criticality accident. Note: This diagram does not in any way depict the actual positions of tanks, pipes, valves, etc. It indicates relative schematic arrangement of vessels and equipment. (Data taken from references 2 and 3.)

When the operator opened valve "A" to drain the contents of tanks No. 3 and 4 into the stainless-steel drum, the enriched uranium solution from tank No. 2 and the connecting piping preceded the test water into the drum. The level of enriched uranium solution in the drum built up to a point permitting initiation of a "critical" nuclear reaction accompanied by the "blue glow" in the solution, which was seen by the operator. The enriched uranium solution flowing from tank

No. 2 into the drum was followed by the test water, which diluted the solution in the drum below the concentration necessary to maintain the "critical" reaction.

While the enriched uranium solution was in tanks No. 1, 2, 3, or 4 the geometry of the solution was such that a nuclear reaction could not take place. The shape of the same solution when in the drum, however, was favorable for a nuclear reaction after a certain depth of solution had been reached. The reaction was stopped by water, which, after the operator left, continued to flow into the drum, reducing the concentration below that necessary to maintain the critical reaction.

There was no explosion, nor would one be expected under the circumstances. However, there was emission of radiation from the nuclear excursion which is believed to have occurred in a pulsing manner with periodic emissions of radiation for a duration not exceeding 4 min.

Three of the men who received the lowest exposure displayed no symptoms of ill effects from their experience; they were released from the hospital on June 26 and returned to work. Five others who received higher exposures remained at the Medical Division Hospital of the Oak Ridge Institute of Nuclear Studies for continued observation and tests. One of these received next to the highest nonfatal exposure from any criticality accident that has occurred in this country to date.

All employees involved in this incident have returned to work.

## *References*

1. AEC Serious Accident Bulletin 134, July 28, 1958.
2. AEC Serious Accident Bulletin 136, Aug. 25, 1958.
3. Accidental Radiation Excursion at the Y-12 Plant June 16, 1958. Final Report. July 28, 1958. (Unclassified AEC report.)
4. AEC Press Release ORO 599, July 31, 1958.
5. Nucleonics, 16(11): 138 (November 1958).

Interest continues in the development of mechanical and chemical methods for decladding and dissolving the wide variety of power reactor fuels which are under consideration.

## Mechanical Processing

For many of the proposed fuels it would be desirable to remove the cladding material mechanically. There are two types of mechanical processing: disassembly and dejacketing. *Disassembly* is the separation of structural components from active individual fuel pins, rods, or plates and will probably be done at the reactor site. *Dejacketing* is the removal of the cladding metals used to contain fissionable and fertile material in the individual pins, rods, or plates and will probably be carried out at the reprocessing plant. With heterogeneous fuel elements some form of disassembly may always be required. However, experience with dejacketing and active core cutting has been limited, and much development work must be done before mechanical exposure and cutting of core materials becomes competitive with chemical dissolution of cladding materials and/or cores.

Mechanical processing offers the important advantages of smaller aqueous waste volumes, the use of less corrosive reagents for dissolving the fuel material when the difficult-to-dissolve cladding is removed, and increased plant capacity in the absence of dissolved cladding material to process streams. With some proposed fuels, mechanical removal of jackets makes continuous fuel dissolution possible. Some of the disadvantages are the problems arising from radiation-induced slug distortion and the use of bonding agents. Operating costs are high because of the complex machines and buildings needed for removal operations and the necessity for maintaining sealed and possibly chemically inert cell atmospheres. Problems of containment and cleanup of the water, air, or inert gas used as the working medium must be solved along with development of production machines that can be operated and maintained remotely.

Culler and Blanco[1] reported at Geneva that of the many mechanical dejacketing methods studied, rolling, milling, extrusion, abrasive cutting, electrical discharge cutting, and shearing are effective for unbonded or NaK bonded fuels. Only rolling and shearing appear applicable to metallurgically bonded fuels.

In work at Hanford[2] a circular saw operating at 16,000 linear ft/min was satisfactory for cutting bundles of stainless-steel rods and bundles of ceramic-filled stainless-steel tubing. Recent studies have shown that a speed of 22,000 linear ft/min is required to cut massive stainless-steel fuel elements.

## Chemical Dejacketing

Selective chemical dissolution of fuel jackets and structural components is an attractive alternate to mechanical dejacketing or complete dissolution. The fuel cores thus exposed can be dissolved by another reagent in a second step. The principal jacket materials are aluminum, zirconium or Zircaloy, and stainless steel.

### Removal of Zirconium and Zircaloy Jackets

A flow sheet for dissolving Zircaloy or zirconium jacketed uranium dioxide reactor fuels in 9*M* aqueous hydrofluoric acid has been demonstrated at ORNL[1] (Fig. 2) with a uranium loss of 0.5 per cent. Hydrofluoric acid was found to remove zirconium cladding effectively at low temperatures.[3] Data obtained at 30°C are shown in Fig. 3.

In the Zirflex process Zircaloy and Zircaloy-2 jackets are selectively dissolved in aqueous ammonium fluoride or in mixtures of ammonium fluoride and ammonium nitrate.[4] The latter are preferred since they result in less evolution of hydrogen. These solutions attack austenitic stainless steels (container materials) only slowly, in contrast to the media (e.g., hydrofluoric acid or hydrofluoric–nitric acid mixtures) generally used for dissolving zirconium. In boiling 6*M* ammonium fluoride the rate of

penetration of Zircaloy-2 is nearly 100 mils/hr, whereas that for typical austenitic stainless steels is only about 0.5 mil/month.

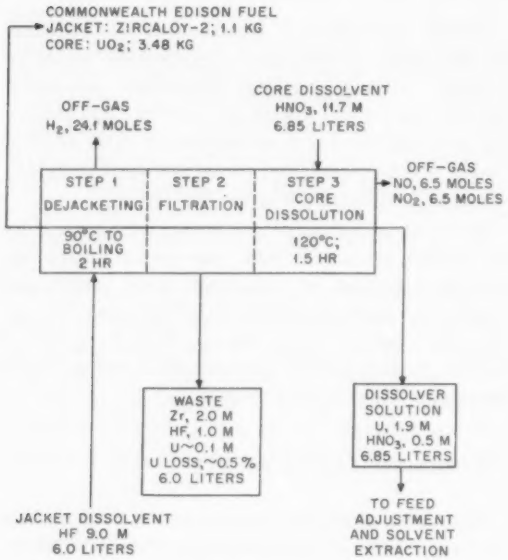


Fig. 2—Hydrofluoric acid process for dejacketing zirconium jacketed fuels. (Data taken from reference 1.)

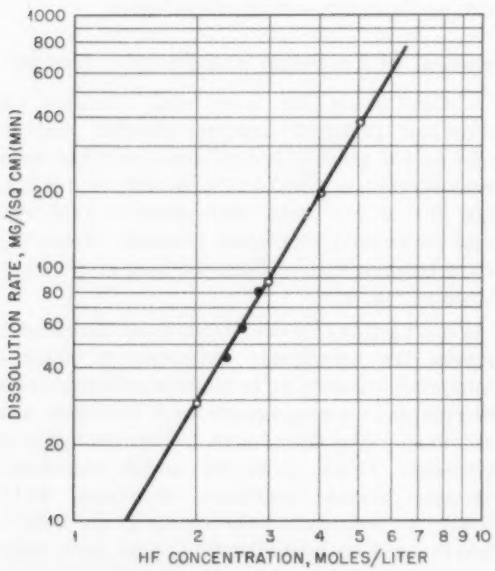


Fig. 3—Dissolution rate of zirconium in hydrofluoric acid at 30°C. ●, zirconium salt present. ○, HF only; no Zr(IV). (Data taken from reference 3.)

Such a process has been applied to the decladding of Pressurized Water Reactor (PWR) blanket fuel elements[5] using boiling 6*M* ammonium fluoride–1*M* ammonium nitrate. A 30-mil Zircaloy-2 jacket was completely dissolved in about 2 hr with a uranium loss of less than 0.02 per cent (probably represents minimum loss).

The application of this process to power reactor fuels, particularly to Enrico Fermi reactor fuel, is being studied at Savannah River.[3] This fuel consists of pins 0.158 in. in diameter by 30 in. long. The alloy is 10 wt.% molybdenum–90 wt.% uranium and is clad with 4 mils of zirconium. It was possible to remove this clad in about 10 min in boiling 3*M* ammonium fluoride. Prolonged heating of the exposed uranium-molybdenum with fluoride solution increased the uranium loss as an insoluble fluoride. The mole ratio of fluoride ion to zirconium ion must be greater than four to maintain reasonable rates of dissolution of the zirconium.

Figure 4 illustrates the procedure involved in preparing a low-fluoride solvent-extraction feed solution from a Zircaloy-clad fuel element having a composition approximating that of the uranium dioxide fuel element proposed for the Plutonium Recycle Test Reactor (PRTR) at Hanford. The amount of uranium that will be converted to insoluble fluorides during the decladding operation cannot be clearly determined at this time. A simple approach to the dissolution of the solid fluoride produced in the decladding step is dissolution in a mixture of aluminum nitrate and nitric acid. The resultant solution is blended with bulk feed. Experimental evidence indicates that the percentage plutonium losses will be less than the uranium losses.

## Removal of Stainless-steel Jackets

The Sulfex process (Fig. 5) has been proposed for removal of the type 304L stainless-steel jacket from the Yankee Atomic Power Reactor (YAPR) fuel elements[1] in boiling 6*M* sulfuric acid followed by dissolution of the uranium dioxide core in 8*M* nitric acid. Dissolution rates of 4.7 mg/(sq cm)(min) have been measured for type 304L stainless steel in 6*M* sulfuric acid. The dissolution rates of uranium dioxide, uranium metal, and 10 wt.% niobium–90 wt.% uranium core materials in sulfuric acid are low enough to predict a negligible loss to the dejacketing solution.

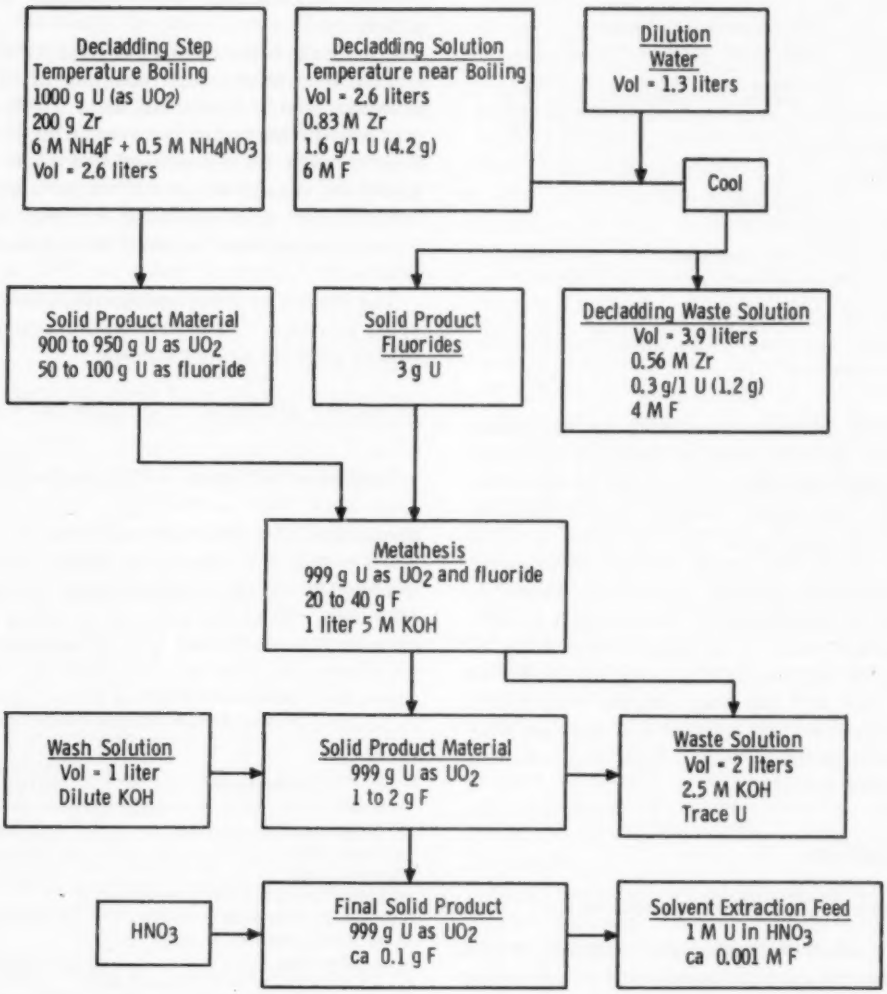


Fig. 4—Preparation of low fluoride feed solution from zirconium-clad fuel element. (Data taken from reference 3.)

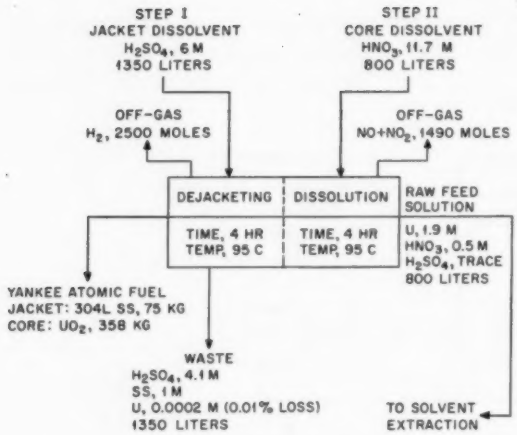


Fig. 5—Sulfex process for dejacketing stainless-steel jacketed fuels with dilute sulfuric acid. (Data taken from reference 1.)

The Sulfex process is probably not applicable to a fuel element with a sintered uranium dioxide–stainless-steel core clad in stainless steel, e.g., the Army Package Power Reactor (APPR) fuel, because of the difficulties involved in recovery of the small amount of uranium dioxide from the solution. In addition, radiation may promote dissolution of the uranium dioxide in the sulfuric acid. In an experimental dissolution with 6*M* sulfuric acid of a highly irradiated (40 per cent $U^{235}$ burn-up) sample of an APPR fuel element, 94 per cent of the uranium dissolved, compared to only 0.5 per cent from an unirradiated sample.

## *Dissolution*

### Simultaneous Dissolution of Jacket and Core

1. *Zirconium Fuel Elements.* Some of the promising dissolution methods for preparing zirconium-containing fuels for solvent extraction are dissolution in aqueous fluoride–nitric acid mixtures, hydrochlorination (Zircex process), and dissolution in anhydrous hydrochloric acid–ethanol. Less promising possibilities are oxidation followed by a nitric acid leaching of the residue, anodic electrolytic dissolution in hydrochloric acid, and dissolution in sulfuric acid–hydrofluoric acid (Sulfex-F process).

The Enrico Fermi reactor fuel (zirconium jacketed 10 wt.% molybdenum–90 wt.% uranium alloy) may be prepared for solvent extraction by dissolution in mixed nitric acid and hydrofluoric acid.[1] Both the jacket and the fuel are dissolved in one operation in 2.5*M* nitric acid–0.06*M* hydrofluoric acid. The core dissolved at a rate of about 100 mg/(sq cm)(min). Molybdenum is soluble at uranium concentrations up to 12 g/liter.

Argonne's Experimental Boiling Water Reactor (EBWR) alloy which consists of 93.5 wt.% uranium, 5 wt.% zirconium, and 1.5 wt.% niobium may also be dissolved in mixed nitric and hydrofluoric acids. In a proposed flow sheet the fuel would be dissolved in 3*M* nitric acid–0.06*M* hydrofluoric acid, followed by evaporation to form a concentrated solution for solvent extraction.

The Zircex process has been discussed in previous Reviews.[6,7] The principal reactions in the Zircex process are as follows:

$$Zr(solid) + 4HCl(gas) \rightarrow ZrCl_4(solid) + 2H_2(gas)$$

$$U(solid) + 3HCl(gas) \rightarrow UCl_3(gas) + \frac{3}{2}H_2(gas)$$

Zirconium tetrachloride sublimes at about 300°C, but the vapor pressure of uranium trichloride at this temperature is less than $10^{-11}$ atm. Thus the process involves reaction of metallic zirconium and zirconium-uranium alloys with anhydrous hydrogen chloride at 400 to 800°C to form gaseous zirconium tetrachloride and solid uranium trichloride.[1] The Zircex process may be applicable either as a dejacketing method for oxide core fuels or as a method for complete hydrochlorination of metallic fuels. Laboratory tests on a variety of fuels have yielded the data in Table III-1.

Table III-1 DISSOLUTION RATES FOR A VARIETY OF FUELS BY ZIRCEX METHODS*

| Fuel Material | Dissolution rates,† mg/(sq cm)(min) |
|---|---|
| Zirconium-uranium alloy | 2 to 25 |
| Uranium metal | 0.17 to 20 |
| Thorium metal | 0.17 to 20 |
| 93.5 wt.% uranium–5 wt.% zirconium–1.5 wt.% niobium alloy | 5.3 to 7.9 |
| 10 wt.% molybdenum–90 wt.% uranium alloy | 3 to 24 |
| 2 wt.% niobium–98 wt.% uranium alloy | 0.75 to 0.79 |

*Data taken from reference 1.
†An acceptable rate is > 3.4 mg/(sq cm)(min).

Anhydrous hydrochloric acid–ethanol is a promising solvent[1] for zirconium-, molybdenum-, and niobium-containing fuels and for dejacketing Zircaloy-2–clad oxide fuels. The process requires three steps: dissolution, removal of ethanol by evaporation, and elimination of chlorides by distillation from 8*M* to 10*M* nitric acid. Thorium and uranium oxide cores, which are insoluble in anhydrous hydrochloric acid–ethanol, would be dissolved in nitric acid after removal of an anhydrous hydrochloric acid–ethanol dejacketing solution. Development has been confined to a laboratory scale. Zircaloy-2, uranium, and thorium dissolve in 9.4*M* anhydrous hydrochloric acid–ethanol at 25°C at rates of about 3, 4, and 81 mg/(sq cm)(min), respectively.

2. *Stainless-steel Fuel Elements.* A number of dissolution processes for fuel elements which contain stainless steel have also been studied.[1] The most promising methods at the present time are dissolution in dilute aqua regia (Darex process) and in dilute sulfuric acid (Sulfex process). Other possibilities that have been studied are anodic electrolytic dissolution in nitric acid, carburization of the stainless steel followed by complete dissolution in nitric acid, dissolution in nitric acid catalyzed by chromate ion, dissolution in 14*M* hydrofluoric acid, and dissolution in nitric acid–hydrofluoric acid mixtures.

Conversion of Yankee Atomic fuel pins to an aqueous nitrate solution by a batch-operated Darex system[8] assumes integral dissolution of the 304L stainless-steel cladding and the sintered uranium dioxide pellets of the core in dilute aqua regia, followed by distillation to remove chloride and water. Nitric acid in excess of that required for solvent extraction is also removed.

Batch dissolution of stainless-steel samples in dilute aqua regia with a simple updraft condenser showed a hydrogen ion consumption of 4 moles per mole of stainless steel and a chloride consumption of 0.2 mole per mole. Satisfactory chloride and acid removal was obtained by evaporating the dissolver solution to one-half volume, adding a volume of 15.8*M* nitric acid equal to the original dissolver solution volume, and evaporating to 126°C. Dilution of the product with water produced a solvent-extraction feed containing less than 50 ppm of chloride.

Stainless-steel–based fuels may be dissolved in sulfuric acid or in aqua regia. The use of either of these acids means that dissolver vessels must be constructed of something other than the conventional 18-8-1 steels (18 per cent chromium, 8 per cent nickel, 1 per cent molybdenum). Sulphate solutions containing uranium may be used as feed for conventional solvent-extraction systems after adding nitric acid, but aqua regia solutions must be distilled with nitric acid in order to remove chloride ion before the next stage in processing.

Two methods for dissolving stainless-steel elements directly in nitric acid have been considered:[9] (1) treatment with methane, ammonia, or sodium cyanide at high temperatures to introduce carbon or nitrogen into the steel and thus alter its characteristic structure; and (2) by making the steel element a consumable anode in a nitric acid electrolytic bath.

The type of element that has been considered in the investigations of the first method is a laminar plate about 0.050 in. thick having a dispersed uranium dioxide in a stainless-steel core. Since only about the central third of the thickness of the plate consists of cermet, the problem is essentially that of dissolving stainless steel. Consequently many of the experiments were carried out with stainless steel (18-8-1) alone.

The treatment of 18-8-1 type stainless-steel plate with ammonia or methane at about 1000°C renders the metal more susceptible to dissolution in nitric acid. The rate of penetration (of carbide or nitride) is very slow and the method does not seem to be very suitable, except for the treatment of very thin plates (~0.025-in. thickness).

Stainless steel and stainless-steel–uranium dioxide cermets dissolve readily in nitric acid if an anodic potential is applied. High current efficiencies are obtainable with direct current and moderate efficiencies, with alternating current. A wide range of initial nitric acid concentrations may be used, and dissolution may be carried to the point where large quantities of ferric hydroxide are precipitated. Uranium recoveries are >99.5 per cent. The bulk of the fission product activity is found in solution, but fission product niobium is associated with traces of insoluble residue. The method would be suitable for the dissolution of large pieces of stainless steel (e.g., whole fuel elements) where individual electrical contacts may be made ex-

ternal to the solution; it would not be suitable where large numbers of small pieces have to be held (e.g., in a platinum basket), due to the almost negligible current efficiencies that are obtained in such cases.

3. *Aluminum Fuel Elements.* A fuel which has received consideration for the PRTR at Hanford is an aluminum-silicon-plutonium alloy.[10] The use of the various proposed dissolution processes for this type of fuel was investigated with the following conclusions:

(1) The presence of 11.5 wt.% silicon in aluminum-plutonium alloys results in a very great reduction in the dissolution rate in boiling 8*M* nitric acid containing 0.003*M* mercuric ion. The silicon fails to dissolve and remains as an adherent coating. Dissolution rates in the range of 0.2 to 0.5 mg/(sq cm)(min) were experienced. These rates are unacceptable for a practical process.

(2) Complete dissolution of aluminum-silicon-plutonium alloys can be effected by the use of a nitric acid–hydrofluoric acid system. It is necessary, however, to use at least 3 moles of fluoride per mole of aluminum to maintain an adequate dissolution rate. Under such conditions, stainless-steel corrosion is in the 50 to 150 mils per month range. Further problems with the use of fluoride include handling of dissolved silicon, fate of volatile fluorides, fate of plutonium in silica digestion processes, and testing of subsequent processing steps with the derived feed.

(3) Dissolution of the alloy can be achieved by reacting it with boiling sodium hydroxide solution followed by acidification of the resulting system. The product solutions are colloidal in nature and in limited experiments resisted coagulation.

(4) Although not experimentally verified, the reprocessing of aluminum-plutonium alloy by a number of prospective pyrochemical methods would appear to be very greatly complicated by the addition of silicon to the alloy.

(5) From the chemical processing point of view, silicon is one of the least desirable materials to deal with. If at all possible, its use should be avoided.

## Dissolution of Dejacketed Material

A large number of alloys of uranium, thorium, and plutonium with metals such as zirconium, niobium, molybdenum, chromium, aluminum, and silicon are being considered as reactor fuels.[1] In addition, oxides and mixed oxides of uranium, plutonium, and thorium are receiving increased consideration. If the fuel jackets can be removed mechanically or chemically or the fuel sheared into pieces, dissolution of the irradiated core becomes a separate and possibly simpler feed preparation approach.

Dissolution in nitric acid has been widely reported for dejacketed uranium metal fuels. Dissolution of aluminum reactor fuel elements in mercury-catalyzed nitric acid has been studied. The results of a study of the effect of geometrical shape of aluminum reactor fuel elements on the dissolution rate in mercury-catalyzed nitric acid have been presented by Boeglin and Buckham.[11] Four shapes (round rods, tubes, flat plates, and flattened tubes) were tested at five catalyst concentrations (from $1.5 \times 10^{-6}$ to $7.5 \times 10^{-4}$*M* Hg), and at each of three feed rates (280, 140, and 70 gram-moles of nitric acid per hour).

A mathematical relationship between dissolution rate and feed rate was graphically developed for each shape. At the higher catalyst concentrations, all shapes dissolve at practically the same rate. However, flat plates and flattened tubes are much less dependent on catalyst concentration and at lower catalyst concentrations dissolve over twice as fast as round rods and tubes. Correlation of the dissolution rates of round rods with the rates obtained in previous work on cylindrical uranium-aluminum alloy fuel elements showed very good agreement. A comparison of the dissolution rate obtained in a stainless-steel vessel and that obtained in a glass vessel was made; no appreciable difference was noted.

Studies at Savannah River[3] showed that after decladding, a 10 wt.% molybdenum–90 wt.% uranium alloy dissolved readily in hot nitric acid solutions. Data obtained for dissolution runs at 100°C in 4*M* nitric acid with varying quantities of hydrofluoric acid present are indicated in Table III-2.

One of the problems associated with reprocessing power reactor fuels containing niobium is the very low solubility of niobium in nitric acid solutions resulting in the precipitation of niobium pentoxide. Several experiments were performed in an attempt to find a complexing agent for niobium so that it may be kept in solution in nitric acid–hydrofluoric acid

Table III-2 EFFECT OF FLUORIDE AND ALUMINUM ON THE RATE OF DISSOLUTION OF URANIUM-MOLYBDENUM ALLOY IN 4*M* NITRIC ACID AT 100°C*†

| Dissolving solution | Initial rate of dissolution, mg/(sq cm)(min) | Time for complete dissolution of pin core, hr |
|---|---|---|
| 4*M* $HNO_3$ | 12.3 | ~4 |
| 4*M* $HNO_3$ – 0.0069*M* HF | 40.5 | 3 |
| 4*M* $HNO_3$ – 0.14*M* HF | 70.5 | 2 |
| 4*M* $HNO_3$ – 0.28*M* HF | 99 | 0.7 |
| 4*M* $HNO_3$ – 0.28*M* HF – 0.28*M* $Al(NO_3)_3$ | 18 | 3.5 |

*10 wt.% molybdenum – 90 wt.% uranium.
†Data taken from reference 3.

mixtures.[12] Adding oxalic acid or tartaric acid in a mole to mole ratio (acid to niobium pentoxide) during dissolution was not successful. By separating the niobium precipitate from the dissolver product and then dissolving the niobium pentoxide in hydrofluoric acid (27 to 1 HF to $Nb_2O_5$) and adding tartaric acid in a 1 to 1 mole ratio (tartaric acid to niobium pentoxide) to this solution, the niobium can be kept in solution at room temperature when added to nitric acid or aluminum nitrate solutions. Less than this mole ratio results in reprecipitation approximately ½ hr after the niobium is added to aluminum nitrate solution; 1 to 1 mole ratio solution is stable for at least 48 hr.

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## *Solvent Extraction*

### Purex and Redox Process Improvements, Modifications, and New Applications

Redox and Purex, the principal solvent-extraction processes currently in use, employ as extractants methyl isobutyl ketone in the former and tributyl phosphate diluted with kerosene in the latter. Work continues in an effort to improve these processes and to adapt them to a variety of separations problems.

In the Purex process decontamination is limited by ruthenium and zirconium-niobium activities. However, there is a significant temperature effect. The principal fission product in the uranium and plutonium product streams is ruthenium at 30°C and zirconium-niobium at 70°C. By operating one portion of the scrub section at 30°C and the other at 70°C improved decontamination was realized.[1] In one solvent-extraction cycle followed by an adsorption process, decontamination factors for both product streams were achieved equal to or greater than those normally attained in the two-cycle Purex process.

Another scheme for improving the decontamination from zirconium-niobium and ruthenium activities involves the use of a silica-gel adsorption column for partitioning uranium and plutonium.[2] In the normal Purex first cycle, uranium and plutonium are decontaminated in the 1A contactor and separated in the 1B contactor. Laboratory tests showed that the products could be separated and further decontaminated in a silica-gel column. The 1A organic product stream was passed through the silica gel which had been treated with a plutonium reductant. The reduced plutonium was retained on the gel while the bulk of the uranium remained in the solvent stream and passed through the column. The residual uranium was eluted with Purex solvent and the plutonium with an aqueous solution of nitric acid. Most of the zirconium in the 1A organic product stream was retained by the gel and subsequently eluted with oxalic acid. Decontamination factors realized by the silica-gel treatment were as follows:

| | Zirconium | Ruthenium |
|---|---|---|
| Uranium | 8 | 4 |
| Plutonium | 30 | 1.2 |

Studies of a cyclic ketone, 2-methyl cyclohexanone, as an alternate for the Redox solvent, methyl isobutyl ketone (hexone), showed that a savings in salting agent could be realized.[3] At the feed point the same uranium distribution coefficient was obtained with about 10 per cent less aluminum nitrate and the ruthenium decontamination factor was twice that obtained with hexone. However, the cumulative decontamination factor after three scrubs was only two-thirds of that obtained with hexone.

A Purex type flow sheet has been successfully adapted to the recovery of uranium and neptunium from fluoride ash.[4] The ash, a nonvolatile material remaining after the fluorination of uranium trioxide to uranium hexafluoride, contains approximately 600 kg of uranium and 11 g of neptunium per ton. After dissolution in a boiling solution, 1.8*M* in aluminum nitrate and 1.0*M* in nitric acid, the products were extracted with 15 per cent tributyl phosphate in kerosene. Over two solvent-extraction cycles, neptunium was separated from uranium by a factor of $3.6 \times 10^5$ with the uranium content of the neptunium product being 0.138 g uranium per gram neptunium. Losses to the waste streams were 0.01 per cent for uranium and 0.7 per cent for neptunium.

### Process Applications of Organophosphorus and Organonitrogen Extractants

Most of the organophosphorus and organonitrogen compounds are relative newcomers on the solvent-extraction scene. These reagents are expected to have considerable effect on the future of solvent extraction because they are

liquid reagents which obey the principles of ion exchange. In the previous Review,[5] introductory remarks were presented concerning the structure of these reagents and the mechanism by which they extract ions from aqueous solutions. This Review is devoted principally to process applications. For simplicity the various reagents are identified as follows:

| | |
|---|---|
| Mono-heptadecylphosphoric acid | HDPA |
| Di-2-ethylhexylphosphoric acid | D2EHPA |
| Dihexylhexylphosphonate | DHHP |
| Trioctylphosphine oxide | TOPO |
| Triisooctylamine | TIOA |
| Tributyl phosphate | TBP |

Organophosphorus reagents diluted with kerosene have been demonstrated as satisfactory solvents for the extraction of uranium from incinerator ash leach solutions.[6] The source of the ash was combustible materials from uranium machining areas. They had been burned at 400°C to give an ash containing about 0.16 g of uranium per gram of ash and subsequently leached with nitric, hydrochloric, sulfuric, or phosphoric acids. The organophosphorus reagents were investigated in order to find a substitute for Purex solvent, TBP, which did not satisfactorily extract uranium under all process conditions.

Organophosphorus compounds were satisfactory extractants for nitric, sulfuric, and phosphoric acid leach slurries but produced semistable emulsions when contacted with hydrochloric acid solutions. Mixtures of D2EHPA-DHHP and D2EHPA-TOPO, which exhibit synergistic characteristics, were the most powerful extractants, and HDPA was satisfactory. For the synergistic mixtures, D2EHPA-DHHP, both U(IV) and U(VI) were extracted with equal facility from nitrate solution. Extraction of U(IV) was much poorer from sulfuric and phosphoric acid solutions. The extraction coefficient for HDPA remained unchanged or increased with the reduction of uranium to the (IV) state and was highest for extraction from sulfuric acid solution.

For extraction of uranium from 12*M* hydrochloric acid solution, Commercial Solvents Corp., 9 D-178 amine was satisfactory. Another amine, TIOA, was investigated but proved unsatisfactory because the uranium salt formed a third organic phase. The addition of a long chain alcohol, which has proved beneficial in some cases, did not prevent the formation of a third organic phase.

Stripping of uranium from the organophosphorus reagents was satisfactorily accomplished with an aqueous solution of sodium carbonate, and the addition of a small percentage of ammonium hydroxide increased the rate of phase separation.

Another interesting application of the versatile alkylphosphoric acid reagents was in the direct extraction of uranium from acid leach slurries.[7,8] The normal procedure is to clarify the slurry before the solvent-extraction step. Pilot-plant studies demonstrated the feasibility of direct slurry extraction but revealed extremely high solvent losses when heavy slurries were treated.

Notable advances have been made in the application of the new extractants to the extraction of fission-product wastes, uranium, and plutonium from power reactor fuels. Experimental work has been reported on the recovery of plutonium and uranium from sulfate and nitrate solutions, the recovery of strontium, cesium, and zirconium-niobium from nitrate solution, and the separation of neptunium from thorium.[9]

Uranium and plutonium were extracted from sulfate solutions, produced in the dissolution of stainless-clad fuels, with phosphine oxides, dialkylphosphoric acids, and primary and *N*-benzylamines. Extraction coefficients were low, but usable, in high acid sulfate solutions and were increased by the addition of a small amount of nitrate ion. Plutonium(VI) was stripped from 0.3*M* phosphine oxide in kerosene solution with aqueous sodium carbonate solution with no evidence of plutonium precipitation in the solvent. Plutonium(IV) was extracted strongly from nitrate solution with TOPO, and a synergistic effect was noted with the mixture D2EHPA-TOPO. However, the synergistic enhancement of Pu(IV) extraction was noted only in nitrate solution.

Sodium salts of the organophosphorus acids extracted cesium and strontium activities from dilute sodium nitrate solutions. For extraction of strontium with Na-D2EHPA the separation factor (Sr/Na) was about 2000 at an aqueous pH of 5.0. The best cesium separation factor observed was lower being about 30 for extraction with Na-HDPA from 1 to 1.5 pH solution. Zirconium-niobium activities were extracted from nitrate solution with D2EHPA to a loading limit of 1 mole zirconium per 3 moles D2EHPA.

## Tributyl Phosphate Extraction

### Mechanism Basic Studies

A substantial amount of experimental evidence has been accumulated to show that the extractant in Purex systems is an equimolar TBP-nitric acid complex. It has been postulated that the extraction of uranium with solvents such as tributyl phosphate or trioctylphosphine oxide which do not have a labile (free) hydrogen depends largely on a nitric acid complex. The extraction mechanism involves the replacement by the uranyl ion of two hydrogen ions in the TBP-nitric acid complex.[10,11]

Uranium was extracted from sulfate, chloride, phosphate, and fluoride solutions with a solvent containing TBP-nitric acid. Extraction with a solvent containing pure TBP was either poor or negligible.

The strength of the TBP-uranyl nitrate bond was estimated by an isotopic-exchange method using uranyl nitrate solutions of either depleted or normal uranium. Isotopic exchange was completed in less than 1 min, thereby indicating that uranium is weakly held in the TBP-uranyl nitrate system.

The effect of nitrate ion on the equilibrium distribution of nitric acid between Purex solvent and water was determined by substituting nitrate as sodium nitrate for a portion of the nitric acid in the starting acid solution. The concentration of nitric acid in the solvent was found to be independent of the source of the nitrate ion provided that sufficient hydrogen ions were available for the equilibrium requirements of the TBP-nitric acid complex.

Studies of the distribution of pure nitric acid between aqueous and solvent phases showed that the equilibrium concentrations were dependent on the concentration of associated acid in the aqueous phase. For example, in 7*M* nitric acid roughly 50 per cent of the acid is present as the $HNO_3$ molecule. The presence of a nitrate salt forces the recombination of hydrogen and nitrate ions and, hence, increases the amount of associated nitric acid. The role of the associated nitric acid was further verified by studying the extraction of uranium from sulfate solution with the TBP-nitric acid complex. Uranium was readily extracted. However, the sulfate ion extraction was negligible thus indicating a hydrogen ion-exchange mechanism.

## Degradation of Process Solvents

Process solvents suffer degradation because of chemical and radiation damage. The degradation products are frequently objectionable because they may form insoluble compounds, solvent-soluble fission-product complexes, unstrippable uranium or plutonium complexes, and surface-active agents. A compilation of literature references concerning the degradation of Purex solvent (TBP diluted with kerosene) has been published.[12]

The new organophosphorus extractants are more resistant to radiation damage than tributyl phosphate.[13] The decomposition rate of TBP was about 1 per cent per 30 watt-hr/liter irradiation. Tests showed dibutylphosphonate to be two times and tributylphenolphosphonate six times as resistant to radiation damage as TBP.

The extractants are diluted, usually with kerosene, for process use. Diluent degradation produces unsaturated compounds which may be emulsifiers or complexing agents. Diluents are susceptible to degradation by concentrated nitric acid or nitric-nitrous acid mixtures. The stability of the diluent to the degrading medium was lessened by the presence of aromatic and branched chain hydrocarbons. The degradation products were identified as organic nitro compounds, organic nitrates, nitrosyl compounds, and carboxylic acids.[8]

The principal degradation products of TBP, mono and dibutyl phosphate, inhibit the transfer of uranium from the aqueous and solvent phases, respectively. A sodium carbonate wash suffices to remove these products from used solvent, however, it does not effectively remove diluent degradation products. Treatment of degraded diluent with a phosphorus pentoxide-sulfuric acid mixture effectively removed all of the degradation products. However, this treatment was unsatisfactory for treating Purex solvent because TBP was solubilized by the reagent.[8]

The suitability of solvent for recycle through the extraction process depends upon the effectiveness of the scrubbing operation. Various tests have been developed to determine solvent condition including physical properties and the retention of tracer zirconium. To a large extent these tests have been unsatisfactory either because they bear little relationship to process performance or they were too complicated. A simple coalescence time measurement has been found to provide a very satisfactory test of

solvent condition.[8] The solvent was mixed with the aqueous phase under standardized conditions. The settling time of the dispersion was reproducible and demonstrated effectively the significant differences between solvents having different treatment histories.

### Nuclear Safety and Criticality

Experimental data have been obtained for the critical mass of uranyl fluoride solution containing uranium[14,15] enriched to 44.6 per cent in $U^{235}$ and to 99.6 per cent in $U^{233}$. Measurements covering a wide range of hydrogen to uranium ratios, were obtained in 15.24- and 6.35-cm-radius cylinders for the unreflected, water reflected, and cadmium shielded cases. Minimum critical masses for the water reflected case are shown in Fig. 6.

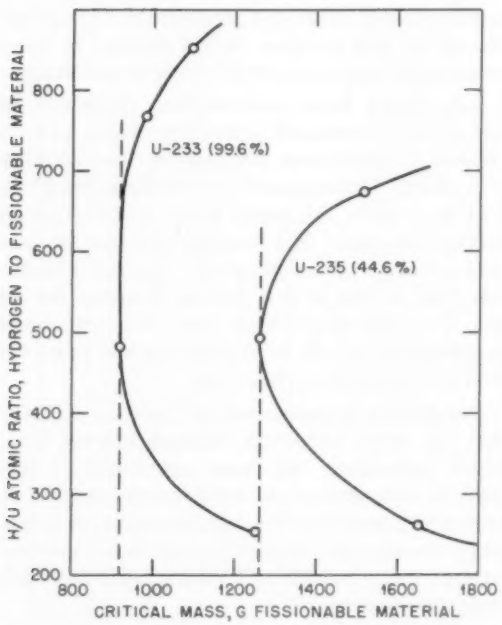


Fig. 6—Critical mass of aqueous uranyl fluoride ($UO_2F_2$) solutions (water reflected 30.48-cm diameter cylinder). (Data taken from reference 15.)

Many of the recent reactor schemes require the use of slightly enriched uranium and hence introduce problems in nuclear safety in an area not previously subjected to intensive study. Data provided in Table IV-1 give the maximum dimensions of water-reflected infinite bodies.[16]

Table IV-1 CRITICAL DIMENSIONS OF WATER-REFLECTED INFINITE BODIES OF SLIGHTLY ENRICHED URANIUM

| Per cent $U^{235}$ in $U^{238}$ | Maximum diam. of infinite cyl., in. | Maximum height of infinite slab, in. |
|---|---|---|
| 1.0 | 18.7 | 10.7 |
| 1.2 | 14.8 | 8.0 |
| 1.4 | 12.5 | 6.4 |
| 1.6 | 11.5 | 5.6 |

Calculations showed that 2 g of boron per liter in the reflecting solution would make safe infinite masses of all shapes to 1.6 per cent enrichment. Homogeneous uranyl nitrate solutions were infinitely safe to 1.8 per cent enrichments, although without nitrate present criticality was possible for solutions above 1.0 per cent $U^{235}$. For dry uranium trioxide powder, infinitely safe conditions existed to 5 per cent $U^{235}$, but for wet powder a critical mass was possible above 1.02 per cent enrichment.

A serious criticality incident occurred at Oak Ridge on June 16, 1958. See pp. 3 to 4.

## *Precipitation Processes*

Interest in the use of precipitation for "head-end" or "tail-end" scavenging procedures as an adjunct to other decontamination processes has continued.

### Decontamination of Plutonium

A laboratory investigation has been made[17] of various aqueous methods, including precipitation, for recovery and purification of plutonium from plutonium-rich reactor fuels. The precipitation of plutonium trifluoride, trioxalate, tetraoxalate, or peroxide is commonly employed in plutonium processing. Since these methods produce a product of high yield and good quality with respect to impurities usually encountered, a study of these procedures was made. Tests were carried out in a solution prepared by dissolving in nitric acid an alloy ingot containing 94.2 per cent plutonium and various amounts of cobalt, zirconium, molybdenum, ruthenium, and cerium. Precipitation procedures gave decontamination factors as shown in Table IV-2.

The data showed that a separation of plutonium from the fission-product element, cerium, is

Table IV-2 DECONTAMINATION FACTORS FOR PLUTONIUM BY PRECIPITATION METHODS

| Element | Plutonium peroxide | Pu(III) oxalate | Pu(IV) oxalate | Pu(III) fluoride |
|---|---|---|---|---|
| Fe | 50 | 33 | 10 | 1.4 |
| Co | 30 | 47 | 95 | 8.6 |
| Zr | 1 | 3.5 | 44 | 1.1 |
| Mo | 140 | 13 | 15 | 1.1 |
| Ru | 14 | 38 | 33 | 36 |
| Ce | 6 | 1 | 1 | 1.1 |

not practical by precipitation methods. However, the oxalate precipitations may have value for concentrating the plutonium product from some other purification system or to effect head-end treatment.

## Removal of Silica from Solutions of Nuclear Fuels

When reactor fuels are dissolved in acids, the solution sometimes contains varying amounts of dissolved and suspended silica that was originally present as impurity in the metal or as silicon in bonding alloy. Silica causes stable emulsions to form and solids to accumulate in the contacting equipment of the solvent-extraction process. At the Savannah River Laboratory[18] a precipitating agent was sought which would remove dissolved silicates or silicic acid, as well as colloidal silica, from aluminum nitrate-nitric acid, solvent-extraction feed solutions. It was necessary that the treatment be simple and economical and that it not interfere with product recovery, fission-product behavior, or waste disposal.

The introduction of gelatin to the extent of about 100 ppm of feed solution effectively flocculated the silica and facilitated its removal by centrifugation. Other soluble proteins reacted similarly, whereas their constituent amino acids did not. The flocculation probably involves hydrogen bonding between the silica and the peptide linkages of the proteins. The treatment with gelatin had no adverse effect on fission-product behavior or uranium recovery. Conventional methods of feed clarification including precipitation of manganese dioxide and the use of synthetic polymeric flocculating agents were found to be ineffective in removing the silica. The introduction of fluosilicates which were subsequently hydrolyzed to silica was effective in clarifying the feed solution, but complete hydrolysis required as much as an 8-hr digestion at the boiling point at fairly high acidities.

## Scavenging of Ruthenium from Purex Uranyl Nitrate Solution

When uranium is recovered from irradiated nuclear fuel by the Purex process, the initial product is a dilute aqueous solution of uranyl nitrate; this solution is subsequently concentrated by evaporation. Ruthenium, zirconium, and niobium are the principal contaminants that remain in the recovered uranyl nitrate. Zirconium and niobium can be removed from the concentrated uranyl nitrate solution by adsorption on silica gel.[19] Laboratory experiments have been performed to develop a method for scavenging ruthenium from concentrated uranyl nitrate solutions.[20] Such a method, combined with the silica-gel treatment for removing zirconium and niobium, might provide an integrated process to remove all three contaminants.

Laboratory tests showed that ruthenium is effectively scavenged from the uranyl nitrate product of the Purex process by the following procedure: Thiocarbanilide and thioacetamide, 0.04 wt.% each, are added to the dilute uranium product stream. The treated solution is then concentrated by evaporation. A solid residue remains in the uranyl nitrate solution during and after the evaporation step. The ruthenium is adsorbed on this solid material and removed from the solution by filtering.

Ruthenium decontamination factors greater than 35 were observed. Uranyl nitrate from which ruthenium had been scavenged by this method showed normal denitration behavior in laboratory tests and the resulting oxide products were normal in composition and functional behavior, i.e., "reactivity" during reduction and hydrofluorination.

The amounts of chemicals used were not critical. Significant ruthenium decontamination factors were observed when the amount of each chemical added was as small as 0.007 wt.%. The presence of organic solvent in excess of its solubility in the unevaporated solution interfered with the ruthenium adsorption; it was not established whether this interference would be eliminated if the excess solvent were completely volatilized or decomposed during the evaporation.

## *Ion-exchange Processes*

Ion-exchange processes have been applied to the purification and recovery of plutonium and neptunium; fundamental studies on the behavior of metal ions in solution are reported; the use of membranes in the Flurex process and the removal of ruthenium and nitrate ion from alkaline solutions are discussed; developments in continuous anion-exchange equipment are indicated.

uct contains 99.9 per cent of the plutonium fed to the process, and concentrations of other cations do not exceed a few hundred parts per million of plutonium.

Neptunium can also be isolated by anion exchange from concentrated nitric acid solutions. A chemical flow sheet for a typical recovery process is presented in Fig. 7. Over 97 per cent of the neptunium in the feed is recovered and concentrated 300-fold in one cycle of ion exchange.

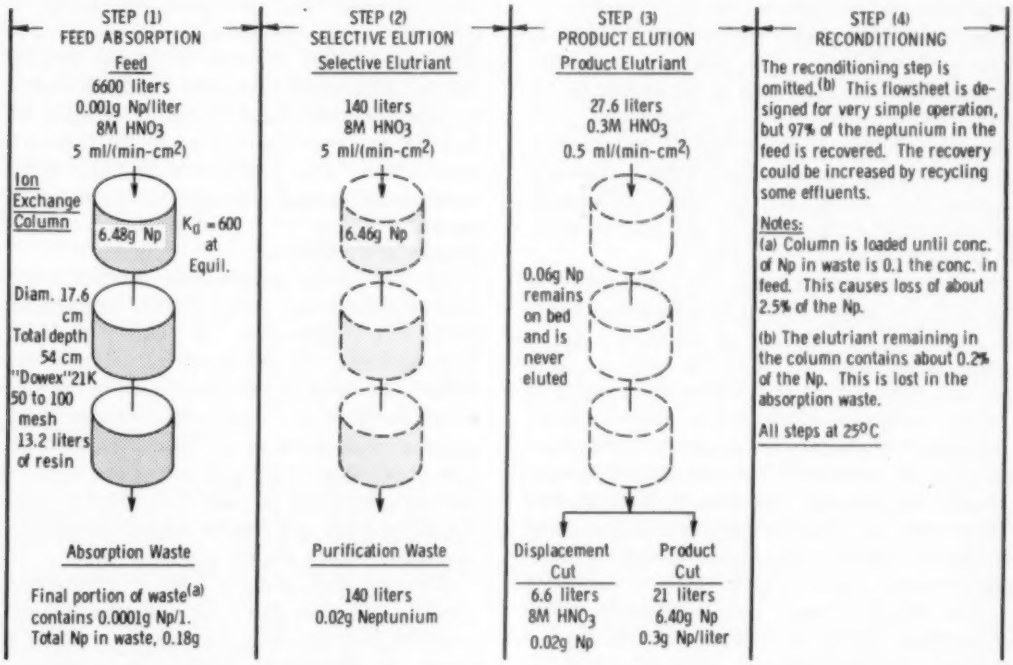


Fig. 7 — Flow sheet for recovery of neptunium by anion exchange. (Data taken from reference 21.)

### Anion-exchange Processes

The purification of plutonium nitrate using a strong base anion resin was described for Geneva by Tober.[21*] The impurities that are removed include many fission-product elements, uranium, iron, chromium, nickel, aluminum, calcium, and magnesium. The plutonium prod-

The anion-exchange behavior of several metal ions in hydrochloric acid, nitric acid, and sulfuric acid solutions, with Dowex-2 has been examined by Bunney et al.[23] Distribution coefficients

$$K_d = \frac{\text{activity per gram of dry resin}}{\text{activity per milliliter of solution}}$$

have been measured for americium, cerium, Mo(VI), palladium, ruthenium, strontium, thorium, U(VI), yttrium, and zirconium. Strontium, yttrium, cerium, and americium did not show any significant adsorption in any of the systems

*A Geneva report, Application of Anion Exchange to the Reprocessing of Plutonium, by J. L. Ryan and E. J. Wheelwright, was received too late for inclusion in this Review and will be covered in the next issue.

studied. Thorium, U(VI), and zirconium show an adsorption maximum at approximately 8*N* nitric acid.

Various separations are shown to be possible in hydrochloric acid solutions. The actinide elements, thorium, palladium, and uranium, are separable by use of concentrated hydrochloric acid, 4*N* to 5*N* hydrochloric acid, and 0.1*N* hydrochloric acid in turn. Also separation of uranium from molybdenum can be accomplished with 0.1*N* hydrochloric acid; removal of molybdenum from the resin column can be achieved with 8*N* to 10*N* nitric acid.

Numerous separations can be obtained from nitric acid solutions. For example, uranium, zirconium and thorium can be separated by 8*N* nitric acid elutions from a column bed, with zirconium eluting first, followed by uranium and then thorium. In addition, ruthenium should be separated from all the other elements studied here by a pass of a 1*N* nitric acid solution through an anion resin bed.

Thorium and uranium will be removed from 0.1*N* sulfuric acid solution by a Dowex-2 resin bed. Subsequent isolation of thorium can be accomplished with a 2*N* to 4*N* sulfuric acid solution. Freiling et al.[24] report the results of an anion-exchange equilibration study in phosphoric acid solutions. The applicability of phosphoric acid solutions to quantitative anion-exchange separations has been investigated by determining the equilibrium distribution coefficients of cesium, strontium, Ce(III), Zr(IV), Te(IV), Ce(IV), Np(IV), Nb(V), Mo(VI), and U(VI) between Dowex-2 resin in the phosphate form and various strengths of phosphoric acid solutions.

The results show that these elements fall into three groups. The first group, consisting of cesium and Te(IV), does not favor the resin phase to any appreciable extent even at 0.1*N* phosphoric acid. The group composed of strontium, Ce(III), and Ce(IV) are weakly adsorbed at low phosphoric acid concentrations ($4 < K_d < 10$). The remaining elements are strongly adsorbed in these solutions ($K_d > 1000$).

## Electrolytic Processes

The over-all efficiency of the Flurex process, an electrodialytic process for the preparation of U(IV) fluoride salts from aqueous uranyl nitrate, depends on the performance of the ion-exchange membranes used. Accordingly, the relative permselectivity, conductivity, and stability of several commercially available ion-exchange membranes have been investigated.[25] Membranes tested include Permutit, Nalfilm, and Nepton in both cation and anion types.

In the Flurex process, a three-compartment electrolytic cell consisting of anode, feed, and cathode compartments separated by anion- and cation-exchange membranes, respectively, is used. Nitrate ion from the uranyl nitrate feed migrates to the anolyte, and uranyl ion migrates to the catholyte where it is reduced at a mercury cathode. Relative permselectivity, conductivity, and hydraulic permeability of the membranes and changes in these properties during long-term exposure of the membranes in process solutions ($UO_2(NO_3)_2$, $UO_2F_2$, $NH_4F$, and HF at temperatures up to 90°C have been determined. The resistance of various membranes in uranyl nitrate solutions and the specific conductivity of anion and cation membranes are available.

All the anion membranes studied exhibited approximately the same degree of permselectivity, i.e., hydrogen ion readily transferred across them. Of the three cation membranes tested, Permutit 3142 membrane is considered most suitable for use in the Flurex process, primarily because of the higher current densities obtainable. Although any of the three anion membranes could be used in the Flurex process, Permutit 3148 and Nepton AR-111 are preferred because of their higher conductivity.

Messing and Higgins[26] have investigated an electrolytic procedure for the removal of ruthenium and nitrate from alkaline waste solutions. In laboratory studies in a nitrate reduction cell, synthetic alkaline waste, 0.55*M* to 4.83*M* total electrolyte, was decontaminated from ruthenium by factors of >210. The nitrate of 3.0*M* waste was reduced to ammonia with current efficiencies of 100 per cent. Power consumption was 4.7 kwh/lb of nitrate reduced.

## Cation-exchange Processes

In two Russian papers[27,28] the separation of aluminum from zirconium by the use of cation-exchange resins is described. The separation is based on the varying exchange capacities of the cations from varying acid concentrations. Zirconium, in comparison to aluminum, should be adsorbed using higher acid concentrations. The adsorption of zirconium on the following

cation resins was determined: sulfocarbonate, Wofatit P, Cation KU-1, SBSR, and MSF-1. On the basis of recovery data it was shown that the separation of aluminum from zirconium is aided by pretreatment of the resin.

Ruthenium and zirconium-niobium are the principal contaminants that remain in the solution of recovered uranium after one cycle of purification by the Purex process. Zirconium-niobium may be removed by passing the solution through a bed of silica gel at 90°C. Prohaska[22] has studied adsorption of ruthenium by ion-exchange resins. After a preliminary treatment with thiourea, at least 90 per cent of the ruthenium remaining in the product uranium stream from the Purex process can be removed by ion exchange with "Amberlite" IRC-50 resin.

## Developments of Continuous Ion-exchange Equipment

Recent developments in continuous ion-exchange equipment for AEC applications have been reviewed by Roberts.[29] Continuous ion-exchange equipment has been greatly improved in the last few years, and several types of contactors are described including a Dorr, a Resin-in-Basket, an Infilco, an ORNL-Jury, and the ORNL-Higgins contactor.

1. *Dorr.* A continuous contactor was put on the market by the Dorr Co. a few years ago. It operates with solution upflow in both sections, with two fluidized beds in series in the softening (sorption) sections, and with the fluidized bed in the regeneration (desorption) section broken into several subsections by so-called "constriction plates." The use of fluidized contact severely limits the number of stages available in a reasonable height and this contactor seems applicable only where a few theoretical stages are required. Careful hydraulic balancing of this contactor is necessary.

2. *Resin-in-Basket.* The Anaconda Resin-in-Basket contactor plant was developed by the AEC for resin-in-pulp operation. The basket contactor eliminates the filtration step usually necessary to avoid plugging ion-exchange beds with the clay slimes present in western uranium ores. The pulp is fed to neoprene-lined steel troughs fitted with stainless-steel baskets each containing 15 cu ft of resin. The baskets are dipped up and down in the trough through which the pulp flows. This vertical action keeps the resin fluidized and thus prevents the slimes from filtering out and plugging the bed. The pulp flows from trough to trough in series as the baskets oscillate. The resin does not flow with respect to the earth, but effective continuous-countercurrent contact is achieved by moving the feed and take-off points from one trough to the next in a 14-trough time cycle.

Although basket resin-in-pulp operation has achieved its objective satisfactorily, it is basically an inefficient method of ion-exchange contacting. It is also a high-capital-investment operation compared to some other systems.

3. *Infilco.* Infilco, Incorporated, and Techmanix Corporation cooperated in designing and operating a resin-in-pulp uranium recovery pilot plant using a mixer-settler contactor. The Infilco contactor might be expected to have a contacting efficiency comparable to the Dorr contactor (better than the basket system), with perhaps some physical advantage from the horizontal arrangement of the stages. It appears to require careful balancing to control resin inventory per stage and resin flow between stages, although the pilot plant was reported to be "noncritical in adjustment."

4. *ORNL-Jury.* This contactor is similar to previously proposed gravity-operated moving-bed contactors except for the feature of a hydraulic ram. The resin moves in the working column as a dense bed, i.e., with the particles maintaining fixed positions relative to each other. The resin is moved down the working column by gravity and by the force exerted by the hydraulic ram. Careful hydraulic balancing is necessary for proper operation of this contactor. Carefully designed low-solution-velocity take-offs are required to prevent the resin from jamming around the exits.

The Jury contactor has not yet reached the stage of development of the other contactors described either in operating experience or in size.

5. *ORNL-Higgins.* This contactor combines the high-throughput, low-HETS advantages of fixed-beds with the operational advantages of continuous-countercurrent flow. It has been tested in sizes up to 20 ft high and up to 3 ft in diameter, and it has been rather fully described in earlier literature.

## *Volatility Process*

Development has continued of various aspects of volatility processing, i.e., processes in which fluorination is used to convert uranium to volatile uranium hexafluoride and decontamination is subsequently effected by distillation or by absorption techniques. Information is included in this Review on fused-salt processing of zirconium alloys and of Aircraft Reactor Experiment (ARE) fuel, on the chemistry of plutonium hexafluoride, on large-scale fluorine production, on studies of the ignition of uranium in interhalogens, and on a new process which combines aqueous dissolution and fluid-bed calcining with fluorination techniques.

### Fused-salt Processing

Developments of fluoride volatility process were summarized in two Geneva papers.[30,31] Applications to uranium, uranium-zirconium alloy and uranium-plutonium alloy fuels were discussed.

Complete phase equilibria in the systems $NaF-ZrF_4$, $UF_4-ZrF_4$, and $NaF-ZrF_4-UF_4$ have been reported.[32]

The decontamination of equipment that had been used for fused fluoride salts was investigated at Oak Ridge.

The decontamination methods studied included barren salt flushes, 0.5*M* ammonium oxalate solution, 5 wt.% nitric acid–5 wt.% aluminum nitrate solution, and 10 wt.% sodium hydroxide–2.5 wt.% hydrogen peroxide–10 wt.% sodium tartrate solution.[33] Salt flushes were relatively ineffective. Ammonium oxalate solutions at about 100°C dissolved sodium fluoride–zirconium fluoride and removed much activity. The nitric acid–aluminum nitrate solution was required to remove a metallic scale from Inconel equipment as the result of contact with hydrofluoric acid, fluorine, and uranium hexafluoride at 600°C. The peroxide tartrate solution was particularly effective in decontaminating descaled reactors and equipment exposed to gaseous reactants.

Considerable information has been made available on the processing of ARE fuel.

The ARE was a circulating fuel reactor which used a molten mixture of fluorides as the fluid fuel. This reactor has been described previously in detail.[34–37] It was operated at various power levels up to 2.5 Mw. The fuel mixture consisted of 53.09 mole % sodium fluoride, 40.73 mole % zirconium tetrafluoride, and 6.18 mole % uranium tetrafluoride. This fuel is very similar to the fused fluoride mixture produced by the dissolution of irradiated zirconium-uranium fuel alloy in fused sodium fluoride–zirconium tetrafluoride.[38,39]

The uranium in the ARE fuel was recovered as the hexafluoride in the fluoride volatility pilot plant at Oak Ridge.[40] This installation has been described by Milford.[41] The processing of this fuel consisted in sparging fluorine gas through the molten salt at 650°C to volatilize the uranium as the hexafluoride. The uranium hexafluoride was then absorbed on solid sodium fluoride beds at 100°C and desorbed in a stream of fluorine as the temperature was raised to 400°C. Laboratory data have indicated that this procedure gives beta-gamma decontamination factors for the entire process in excess of $10^6$.

The irradiated fused salt from the ARE used as the feed to the pilot plant contained 22.8 wt.% sodium fluoride, 69.5 wt.% zirconium tetrafluoride, and 7.7 wt.% uranium tetrafluoride. The activity level was about $5 \times 10^6$ gross gamma counts per minute per gram of salt.

The entire charge was melted in a hold tank under a nitrogen atmosphere. It was then transferred to the fluorination vessel for processing in a series of six charges. During the processing of the first two batches, some uranium hexafluoride was lost due to leaks in the system. The last four charges, which were processed after the leaks had been repaired, are considered to be representative of the process. Approximately 4 moles of fluorine per mole of uranium in the melt was added over a 4-hr period at a temperature of 600 to 650°C. After the fluorination, the amount of residual uranium in the melt was less than 0.03 per cent of that present initially. The barren salt was then transferred to a disposable waste container where it was allowed to solidify.

The uranium hexafluoride was passed through the first absorber filled with solid sodium fluoride at 100°C. Approximately 2 mc of gamma activity was collected by the absorber for each gram of fused salt. The salt itself contained about 2.5 curies of gamma activity both before and after fluorination.

Fluorine was passed through the bed at 400°C to desorb the uranium hexafluoride, which was

passed to the second absorber. When the series of runs had been completed, the first absorber contained about 28 g of uranium and the second, about 16 g. The amount of uranium retained by the absorbers appears to be independent of the amount of uranium hexafluoride processed.

The decontaminated uranium hexafluoride was collected in the cold traps, which were later heated so that the liquid product could be drained into receivers. The decontamination from fission products appeared to be complete. The product recovered was 96.9 per cent of the uranium in the feed, with only 0.01 per cent in the waste salt. Most of the remainder was found in the equipment in a recoverable form.

A process for recovery of uranium and thorium from a fused $LiF-BeF_2$ reactor fuel has been proposed.[9] Fluorination is used to remove uranium from the salt as uranium hexafluoride. Liquid hydrofluoric acid with about 5 per cent water is used to dissolve the bulk of the salt components. Polyvalent fission products tend to have low solubilities and therefore are left behind.

## Chemistry of Plutonium Hexafluoride

Application of fluoride volatility processing methods may be made to reactor fuels containing plutonium. A laboratory study has been made of the fluorination in a flow system of plutonium tetrafluoride by elemental fluorine to form plutonium hexafluoride. The effect of temperatures in the range 100 to 600°C and of fluorine partial pressures from 0.25 to 1.0 atm were examined.[42]

The fluorination rates of uranium tetrafluoride–plutonium tetrafluoride mixtures were investigated.[43] Results indicate that the conversion rate of uranium tetrafluoride to the hexafluoride by elemental fluorine is not affected by the presence of plutonium tetrafluoride. However, the rate of plutonium hexafluoride formation may be decreased due to its reduction by uranium tetrafluoride.

Fluorination rate studies were also conducted on uranium dioxide. Short fluorinations at low temperatures with elemental fluorine appear to produce uranium hexafluoride directly, whereas longer periods of exposure and higher temperatures produce uranyl fluoride as an intermediate compound in the reaction.

The thermal decomposition of plutonium hexafluoride has also been studied. The stoichiometry of the decomposition reaction at 300°C was investigated by several methods which showed the reaction products to be fluorine and plutonium tetrafluoride.

## Uranium Ignition Studies

As a result of an explosion and fire in the Fluoride Volatility Pilot Plant[44] at BNL in May 1957, a program was initiated to study the ignition of metallic uranium in bromine trifluoride systems. Previous work at ANL[45] had shown that uranium exposed to bromine trifluoride vapor above 150°C ignites within a few minutes. No ignitions took place, however, when the metal remained submerged in liquid bromine trifluoride.

The current studies at Brookhaven[46–48] are an extension of the Argonne work, and the experimental techniques employed are similar. Samples of the uranium were suspended on a needle thermocouple in a cell which could be filled with liquid or vapor from bromine trifluoride solutions. The solutions were primarily bromine trifluoride to which varying amounts of uranium hexafluoride, bromine, and bromine pentafluoride had been added. Three different types of uranium samples were used: (1) approximately $\frac{7}{32}$-in. cubes weighing about 3 g, (2) approximately $\frac{5}{16}$-in. cubes weighing about 9 g, and (3) chips from lathe and milling operations, each sample weighing from 1 to 3 g. The cubes were machined from alpha-rolled bar stock, and the chips were from alpha-rolled, beta-quenched uranium slugs. The ignitions were observed through $\frac{1}{2}$-in. quartz windows, and appropriate instrumentation was provided for recording temperature and pressure. The apparatus was surrounded by blast shielding to protect the operators.

The results of the studies with uranium cubes were similar to those of the Argonne work. The uranium ignited on exposure to pure bromine trifluoride vapor after a few minutes at temperatures above about 150°C. The addition of 4 or 5 mole % of uranium hexafluoride to the solution reduced the ignition temperature in the vapor phase to about 115°C. In no case did ignition occur while the uranium was immersed in the liquid, and it was found that immersion in the liquid would quench the burning if the metal temperature had not risen above 250°C. At higher temperatures the metal continued to burn in the liquid phase.

The uranium chips ignited immediately in pure bromine trifluoride vapor at temperatures as low as 25°C, probably as a result of their high specific surface area. Minor detonations occurred in several instances, and in one case a 3-g sample of chips exploded violently.

Additional studies are in progress on the behavior of chips, using solutions containing uranium hexafluoride. Provisions are being made to obtain high speed movies of the ignitions and detonations.

## Fluorine Production

The use of fluorine is common to most of the volatility processes under consideration. A paper by Huber et al.[49] prepared for Geneva on the large-scale manufacture of fluorine is therefore of interest in this connection.

Fluorine plants capable of multi-ton daily output rates are installed at all of the gaseous diffusion plants in the U. S. Atomic Energy Program. These plants have been developed to a reliability that provides on-stream efficiencies as high as 98 per cent. The plant controls are centralized, and a single operator attends a common central control room for both fluorine and uranium hexafluoride production.

A description is given of a production unit with a capacity of 7600 lb of fluorine per day. This plant is a functionally independent unit which consists of forty 6000-amp, medium-temperature, water-cooled, electrolytic cells. The cells are series-connected electrically, with direct current supplied from two mechanical rectifiers of 6000-amp, 225-volt rating. Production control is provided by means of voltage regulation from a central control.

Hydrogen fluoride of 99.95 per cent purity is received in 10,000-gal railway tank cars and is stored in 12,000-gal tanks which are remote from the production area. Liquid transfer to the manufacturing area is accomplished with a regulated pressure of dry nitrogen. Gaseous hydrogen fluoride is fed continuously to all cells from a central vaporizing station. The delivery rate of hydrogen fluoride make-up is controlled automatically at each cell by means of an electrolyte level-measuring probe.

Fluorine and hydrogen production headers are maintained at pressures only slightly exceeding atmospheric. A five-stage centrifugal blower discharges fluorine at 2.5 lb/sq in. gauge for use in the fluorination system. The compressed fluorine flow is refrigerated in partial condensers, which are operated at approximately −110°F to reduce the hydrogen fluoride content to about 4 per cent. The condensed hydrogen fluoride is returned to the vaporizing station for reuse.

Table IV-3 FLUORINE COST ANALYSIS*

| | Dollars/lb fluorine |
|---|---|
| Hydrogen fluoride, $0.20/lb | $0.240 |
| Potassium bifluoride, $0.26/lb | 0.015 |
| Power, $0.00038/kwh | 0.040 |
| Steam, water, air, nitrogen, etc. | 0.020 |
| Labor (includes 18 per cent overhead): | |
| Operation | 0.025 |
| Maintenance | 0.040 |
| Laboratory and supervision | 0.040 |
| Maintenance materials | 0.040 |
| Operating cost | $0.460 |
| Amortization | 0.072 |
| Total | $0.532 |

* Data taken from reference 49.

Table IV-3 presents costs which might be achieved with a plant such as described in this paper. Capital costs are estimated at $4,000,000. Twenty-year amortization of this facility would amount to a depreciation rate of $0.072/lb of fluorine.

## Process Combining Aqueous Dissolution and Fluorination Techniques

A new reprocessing scheme which combines aqueous dissolution with fluorination and fluidization techniques is under study at ANL.[43] This process, which is called the ADF process (aqueous dissolution, fluid-bed drying and fluorination/fluidization), involves the dissolution of irradiated fuel in an appropriate aqueous medium, the calcination of this medium to a mixture of dry oxides, and the fluorination of these oxides to uranium and plutonium hexafluorides. A simplified diagram of the scheme is shown in Fig. 8.

The irradiated fuel is dissolved in an aqueous solution selected on the basis of a particular fuel-element composition. The solution is then subjected to a calcination process in which the uranium, plutonium, fission products, and other elements in solution are converted to a mixture of dry oxides. Uranium trioxide and plutonium

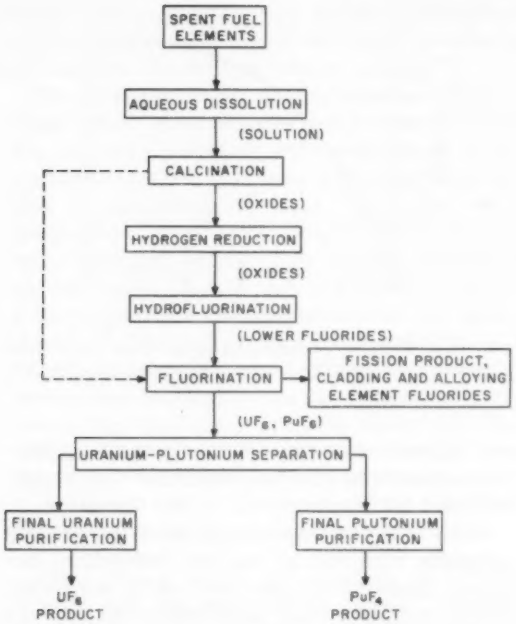


Fig. 8 — Combined aqueous dissolution-fluoride volatility scheme (ADF process). (Data taken from reference 43.)

dioxide are expected to be formed in this operation. The oxide mixture is then fluorinated. This may be done either by the conventional feed-material sequence of hydrogen reduction followed by fluorination with hydrogen fluoride, then with elemental fluorine, or the calcined product may be fluorinated directly. It is expected that these solid-gas reactions would be carried out in fluidized-bed reactors.

## *Pyrometallurgical Processing*

Progress continued to be made on development of pyrometallurgical processes for the undelayed processing of fissile and fertile materials discharged from reactors. The reduction of processing costs which these processes offer results from the ability to process material shortly after discharge from the reactor and from the elimination of chemical conversions. During the last review period, several interesting papers in pyrometallurgical processing were prepared for the Geneva conference. Encouraging progress is reported on several types of pyrometallurgical processes.

### Melt Refining

The melt-refining process* is being developed for EBR-II fuel for incorporation into a closed fuel cycle. The recovery and refabrication operations of this fuel cycle will be carried out in a pilot plant adjacent to the EBR-II reactor. The design of this plant was described by Levenson et al.[50] at the Geneva meeting. Schematic representations of this plant were previously given in the third Review.[51] It is the purpose of the EBR-II pilot plant to obtain the data necessary to determine the technical and economic feasibility of pyrometallurgical processing and of a complete fuel cycle based thereon. EBR-II will be the first reactor in the U. S. Power Demonstration Program to operate on a closed fuel cycle.

The authors asserted[50] that in a nuclear power economy the problems of heavy isotope build-up ($U^{236}$, $U^{237}$, $Pu^{240}$, etc.) cannot be ignored but must be solved by the development of suitable fuel cycles. A similar point of view was taken by Arnold[52] who discussed radiation problems associated with heavy isotope build-up at Geneva.

A Geneva paper by Roesch[53] on theoretical estimates of surface dose rates for combinations of plutonium isotopes which result for various irradiation levels also supports the viewpoint that remote fabrication of these alloys is mandatory regardless of the degree of fission-product separation achieved. The composition of plutonium as a function of irradiation is shown in Fig. 9, and various components of the dose rate as function of irradiation are shown in Figs. 10, 11, and 12. The chief practical conclusion of this report is that there is an advantage of smaller total dose rate if plutonium is processed immediately after its purification from other radioactive materials. If this is done, the main dose rate will come from neutrons emitted during spontaneous fission. In general, the total dose rate will be so high as to make manual handling of plutonium very difficult.

Developments in the melt-refining process itself were discussed in a paper by Burris et al.[54] Pressed lime-stabilized zirconia crucibles have been satisfactory as a container

* Irradiated fuel melted in a zirconia crucible and held molten for several hours allowing purification to occur through vaporization and crucible reactions.

material and as a source of oxygen for fission-product oxidation. On a 2- to 5-kg scale, nearly complete removal of cerium initially at concentrations of around 0.6 per cent has been demonstrated with purified metal yields of around 95 per cent. Figure 13 shows the rates of removal of cerium as a function of temperature

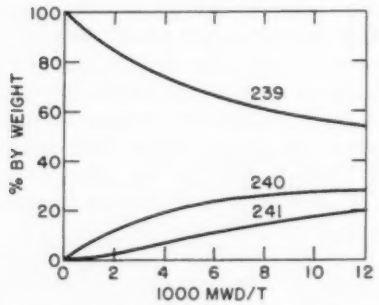


Fig. 9—Composition of plutonium made by reactor irradiation of uranium. (Data taken from reference 53.)

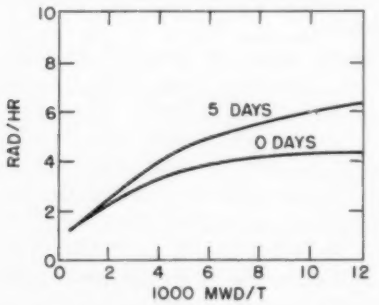


Fig. 10—X- and gamma-ray dose rate from reactor plutonium at 0 days and 5 days after separation. (Data taken from reference 53.)

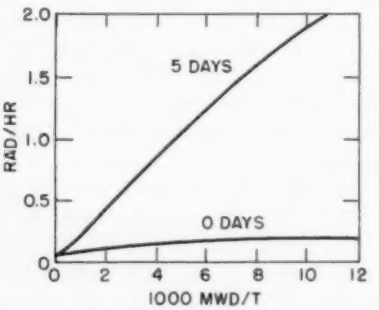


Fig. 11—"Hard" gamma dose rate from reactor plutonium at 0 days and 5 days after separation. (Data taken from reference 53.)

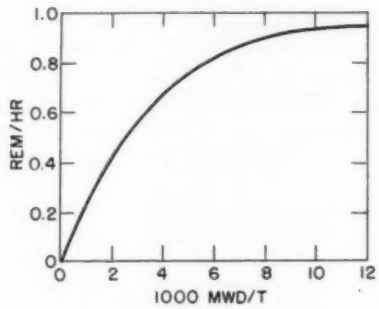


Fig. 12—Neutron r body equivalent dose rate from reactor plutonium. (Data taken from reference 53.)

and crucible material. From these data, practical time-temperature conditions can be established for plant-scale (~ 10 kg) operation.

Work with tracer material shows essentially complete removal of barium, strontium, cesium, cadmium, and rare-earth elements. Nearly complete removal of iodine and the rare gases also occurs. At tracer levels of these elements diffusion through the oxide dross can also be severely limiting.[43] At macro levels evolution of these elements is rapid and complete. The disappearance of iodine is accompanied by the appearance of alkaline-earth iodides in the dross and in volatilized materials.

Removal of cerium in low concentrations (up to 0.06 per cent) by self-slagging reactions (reactions with carbon and oxygen impurities in the uranium) was shown to be an important mechanism if the impurity levels are adequate.[55] This contrasts with the mechanism of removal of cerium initially present at high concentrations and in the relative absence of impurities, in which case cerium diffuses to the crucible wall and reacts there with oxygen provided by the crucible. Cerium compounds formed directly in the melt were removable slowly by liquation or rapidly by filtration through uranium dioxide beds.

The diffusion coefficient of cerium in uranium has recently been determined as a function of temperature over the range,[56] 1170 to 1400°C. An equation relating the diffusion coefficient and temperature is

$$D = 0.02\ e^{-E/RT}\ (\text{sq cm/sec})$$

where E = 15 kcal. The solubility of cerium in uranium varied from 1 to 2 per cent over the

range 1140 to 1345°C. The diffusion coefficient for zirconium in uranium was also reported to be $1.86 \pm 0.87 \times 10^{-4}$ sq cm/sec at 1270°C.

The Pyrometallurgical Refabrication Experiment (PRE) is an engineering development for the remote processing and refabrication of irradiated uranium fuel from SRE type reactors. One of the processes which has been under development is oxide drossing which is synonymous with melt refining. An engineering mockup has been carried out to demonstrate the remote operation and maintenance of the equipment.[57,58] This effort included installation and full-scale operation of remotely operated supporting devices such as molds, metal chargers, ventilation hoods, and transfer equipment. The results have been employed for the design of a facility for work with active materials.

## Processing of Plutonium-rich Fuels

Two papers from Los Alamos, a Geneva paper[59] and an unclassified report[60] present results of pyrometallurgical studies on reprocessing of plutonium reactor fuels. Various methods were surveyed experimentally on a 0.1- to 1-kg scale in order to evaluate their potentialities. Because shielded facilities for handling high burn-up plutonium were not available, all experiments have been conducted with a synthetic fuel, "fissium." This material is an alloy of plutonium containing nonradioactive, typical fission-product elements. Processes investigated include liquation and filtration, oxide drossing, carbide slagging, halide slagging, halide conversion cycles, electrorefining, recrystallization from mercury, and liquid-liquid-metal extraction.

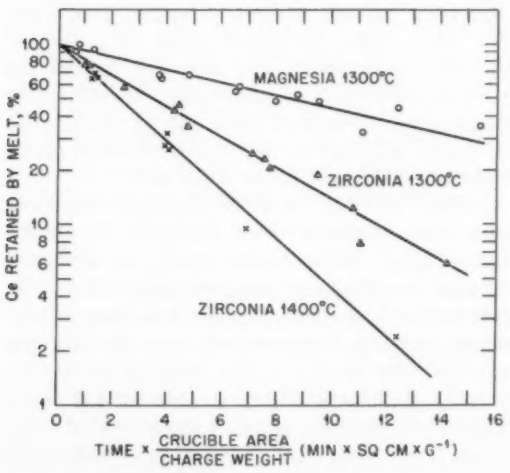


Fig. 13—Cerium removal. (Data taken from reference 76.)

In another Geneva paper,[61] both pyrometallurgical and aqueous methods are discussed.

Efforts within the Plutonium Recycle Project (PRP) continued[62] on the development of efficient chemical processing methods for preparation of plutonium and uranium alloys, recovery of plutonium from irradiated fuel material, and the restoration of the plutonium content in depleted fuel material. Reduction of 98 to 99.8 per cent plutonium and aluminum in the system $PuCl_3$-$KAlCl_4$ was successfully accomplished by the addition of magnesium. Reduction of plutonium trichloride in the absence of aluminum was also effected from an NaCl-KCl eutectic system by magnesium added as a zinc–9 wt.% magnesium alloy. The zinc modifies the density of the metal phase so that it will not float, thereby making possible an open pot process. The zinc also serves to reduce the activity of the plutonium, thus tending to drive the reduction reaction.

The reduction of $UCl_3$ in the KCl-$AlCl_3$-Al system was found to be a maximum (80 to 96 per cent) for $AlCl_3/KCl_3$ ratios of 1.02 to 1.16, decreasing significantly at higher and lower ratios. Similar behavior was noted for $PuCl_3$ reductions, although values were much lower (maximum of 10 per cent reduction). The reduction of plutonium trichloride will probably be further reduced by the presence of uranium in the system.

## Processing of Uranium Oxide Fuel

Studies were continued at Atomics International on the chemical pulverization of uranium oxide pellets by alternate oxidation and reduction cycles.[63] A series of experiments was carried out to determine the oxidation characteristics of various materials. Uranium dioxide pellets from two different vendors and "fissia" (composition simulating that for 1 per cent burn-up) were employed. The fissia appeared to oxidize faster than that of uranium dioxide.

The rate of weight gain of a sintered uranium dioxide pellet of 96.8 per cent theoretical density about 1 cm long and ~1 cm in diameter in air at 1 atm pressure at 385°C was constant

for the first 15 min at $0.75 \times 10^{-5}$ mole/min of oxygen and remained at this value until oxidation was complete.

Electron photomicrographs of powder produced by air oxidation and hydrogen reduction of sintered fissia pellets showed the average particle size to be 0.09 μ. Powder produced from sintered uranium dioxide pellets was comparable in particle size.

In order to study the reprocessing of uranium dioxide fuels under conditions approaching those in practice, fissia pellets (0.8 wt.% simulated fission products) were melted internally by resistance heating. This material was then reacted with air for 3 hr at 385°C. More than 98 per cent of the resultant powder passed through a 400-mesh screen. This indicates that uranium dioxide reactor fuel subjected to high burn-up and temperatures above the melting point will respond to the chemical pulverization process.

Results of decontamination studies using irradiated uranium dioxide are shown in Table IV-4. Appreciable cesium, tellurium, and ruthenium removals are effected, but virtually no removal of rare-earth elements occurs.

Table IV-4 FISSION-PRODUCT BEHAVIOR DURING OXIDATION-REDUCTION CYCLING OF IRRADIATED URANIUM DIOXIDE*

| Oxidation temp., °C | Reduction temp., °C | No. of cycles | Activity lost, % | | | | |
|---|---|---|---|---|---|---|---|
| | | | Te | Ru | Cs | Ce | Re |
| 600 | 600 | 10 | 75 | 94 | 47 | 0 | 0 |
| 600 | 900 | 2 | 80 | 86 | 74 | 9 | 9 |
| 600 | 900 | 4 | 80 | 91 | 73 | 0 | 0 |
| 1250 | 1250 | 1 | 96 | 92 | 94 | 9 | 0 |

* Data taken from reference 63.

A method has been developed for decanning uranium dioxide by oxygen oxidation. After removal of one end of a ½-in.-O.D. stainless-steel can (length not given), the element is suspended upside down in a furnace at 400°C in an oxygen-containing atmosphere. The uranium dioxide oxidizes to $U_3O_8$, disintegrates, and falls from the cladding.

## Liquid-metal Processes

Nearly all pyrometallurgical processes involve purification of fuels in liquid-metal solution. This solution may be the fuel alloy which is melted for processing or which is employed in the reactor directly as a liquid or it may be produced by the dissolution of the fuel in a metal solvent such as zinc, mercury, or cadmium. Purification mechanisms which may be used are selective oxidation or reduction, fractional crystallization, extraction with an immiscible metal solvent, and distillation. Some processes, because of their special importance such as melt refining or because of application to special fuel types, have been discussed previously under separate headings in this section. Others are discussed below.

The development of processes involving fractional crystallization from metal solvents has been reported in the previous Reviews. In common with other pyrometallurgical processes, the fractional crystallization processes possess the desirable characteristic of maintaining the valuable materials mainly in compact metallic forms while processing them with radiation-damage resistant reagents. In addition, these methods promise to be suitable for the processing of a wide variety of fuels and to provide an adequate degree of fission-product separation.

A comprehensive survey and status report on investigations of these processes is the subject of a Geneva paper by Feder and Teitel.[64] The first part of this paper presents physical and chemical data (solubility data for uranium, plutonium, and various fission-product elements in the metal solvents, zinc, bismuth, mercury, lead, and aluminum; nature of intermetallic compounds; coprecipitation phenomena; and thermodynamic data necessary for the development of processes). Specific processes that have been developed using zinc (called Pyrozinc processes) and mercury (called the Hermex process) as the metal solvents are discussed in a second part, and possible areas of future application and some unsolved problems are discussed in the third part.

Additional data on zirconium-zinc and uranium-zinc systems were reported by Chiotti and Voigt.[65] More recent work on Pyrozinc process development has been reported.[43] The solubility of thorium in zinc has been determined down to temperatures near the melting point of zinc (420°C). The data lie on an extension of the solubility line obtained at Ames by thermal analysis of more concentrated solutions.[66] An analytical expression of the result is

$$\log_{10} (\text{wt.\% Th}) = 6.551 - 6383/T$$

The solubility at 800°C is around 4 wt.%, which compares with values of 6 wt.% for uranium and 10 wt.% for plutonium. Solubilities of all three decrease rapidly to a few hundredths of a weight per cent at 500°C.

Uranium may be dissolved fairly rapidly in zinc at 800°C. The kinetics of the reaction of solid uranium with liquid zinc is now being studied over a range of temperature in apparatus in which solid cylindrical specimens are rotated at controlled speeds.[43] The reaction rate has been found to be independent of the degree of saturation of the solution but markedly dependent on surface velocity. The temperature coefficient of the reaction rate is small.

Cadmium is also being investigated as a dissolution and purification medium.[43] It has the advantage of being easily contained in ferrous alloys. One intermetallic compound, $UCd_{11}$, isostructural with $(La, Ce, Pr)Cd_{11}$, has been identified. Studies of the uranium-cadmium system and the ruthenium-zinc system are in progress at the National Bureau of Standards.[67]

Chiotti and Voigt in a Geneva paper[65] discussed two liquid-metal purification schemes:

1. Separation of $U^{233}$ from thorium blanket material

2. A liquid-liquid extraction process for decontaminating a molten uranium fuel using molten silver.

The method of separating uranium from thorium has been mentioned in a previous Review.[68] It involves dissolution of thorium in magnesium at 800 to 900°C to produce a 42 wt.% thorium eutectic freezing at 582°C. The uranium is highly insoluble in this eutectic solution and where cooled to around 600°C is almost completely precipitated. The phases are reported for further processing.

At 900°C, protactinium was extracted almost completely from magnesium-thorium eutectic into a uranium-chromium eutectic phase. This is important since a 27-day $Pa^{233}$ isotope of protactinium is the precursor of $U^{233}$. Its extraction with uranium eliminates the need of long decay times. Rare-earth and alkaline-earth metals remained in the magnesium phase, while the iron, chromium, and the noble metals distributed into the uranium phase.

The separated magnesium-thorium phase may be purified by extracting the rare-earth and alkaline-earth metals into a fused-salt system of magnesium, lithium, and potassium chlorides. The possibility of precipitating thorium from magnesium solution as the hydride was described and is also the subject of an Iowa State College thesis.[69] Ninety-two per cent of the thorium was precipitated at 675°C. An equation relating the concentration (mole fraction) of thorium in solution as a function of temperature is

$$\log_{10} \mathrm{Th} = \frac{-4609 \pm 209}{T} + 2.824 \pm 0.208$$

This process is similar in principle to one under development at Argonne for separation of plutonium and uranium, described in a previous Review.[5] Separation of plutonium and uranium is based on the high and low solubilities of plutonium and uranium, respectively, in magnesium-rich zinc alloys.

The use of molten silver for extracting fission products from molten uranium results in fission-product distribution similar to that encountered in other pyrometallurgical processes.[67] Rare earth and alkaline earths are extracted while the noble metals such as ruthenium and molybdenum remain in the uranium phase. Cerium and zirconium behavior which had been erratic was reexamined. Results appear to have been erratic because of oxidation effects which result in cerium removal as the oxide and zirconium removal as the carbide. Carbon and oxygen impurity levels were sufficiently high for these reactions to occur to a significant extent.

If present, plutonium would also extract into the silver, distribution coefficients on a weight basis varying from 20 to 40 in favor of the silver phase in contact with a uranium phase initially 0.2 per cent in plutonium. Regeneration of the silver phase can be effected by contacting with molten silver chloride at 1000°C. Removal of cerium and zirconium from the silver was complete (as would be the removal of plutonium if present).

Work on both processes is in an early laboratory stage and many steps remain to be studied

along with container materials and the engineering operations involved.

The pyrometallurgical process most extensively investigated by the British is a liquid-liquid extraction process in which molten calcium is used to extract fission products from molten uranium and uranium-plutonium alloys in tantalum crucibles. Data for this process, reported at the Geneva meeting in a paper by Martin, Jenkins, and Keen,[70] are presented in Tables IV-5 and IV-6. For those fission products studied, final fission-product distribution is similar to that resulting from melt refining; i.e., noble fission products and plutonium remain in the uranium phase, whereas the highly reactive fission products such as the rare earths, and barium and strontium will be extracted by the calcium. Volatilization is also an important decontamination mechanism.

Table IV-5 DISTRIBUTION OF PLUTONIUM, URANIUM, AND CERIUM BETWEEN CALCIUM AND VARIOUS ALLOY PHASES AT EQUILIBRIUM AT 1120 TO 1235°C

| Alloy | Constituent | Distribution coefficient* |
|---|---|---|
| U/Pu/Ce | U | 0.0043 ± 0.0015 |
| U/Pu/Ce | Pu | 0.0073 ± 0.0006 |
| U/Pu/Ce | Ce | 11.1 ± 1.1 |
| U/Ce | Ce | 9.5 ± 0.7 |
| U/Ce† | Ce | 9.3 ± 0.3 |
| U/Ce‡ | Ce | 9.4 ± 0.2 |

* Weight per cent in calcium phase/weight per cent in uranium phase.

† Calcium phase poured with alloy phase frozen (1100°C).

‡ High-frequency heating graphite susceptor.

Table IV-6 DISTRIBUTION OF FISSION PRODUCTS BETWEEN MOLTEN CALCIUM AND URANIUM OR URANIUM-PLUTONIUM ALLOY

| Element | Distribution coefficient* | Per cent volatilized (1 hr at 1200°C) |
|---|---|---|
| $Cs^{137}$ | 0.05 to 0.11 | 60 to 95 |
| $Sr^{90}$ | 3.2 to 12 | 6 to 29 |
| $Y^{90}$ (Sr daughter) | 2.5 | |
| $Ba^{140}$† | Very high | 2 |
| Mo | < 0.005 | |
| Ru | $< 1 \times 10^{-4}$ | |
| $La^{140}$ | 50 to 100 | |
| Ce | 9 | |

* Weight per cent in calcium phase/weight per cent in uranium phase.

† The solubility of barium in cerium is < 0.01 per cent.

As shown in Table IV-5 distribution coefficients for plutonium and uranium did not vary either with concentration over the range 0.01 per cent to 20.4 per cent plutonium in uranium, or with temperature in the range from 1120 to 1235°C. Similarly, distribution coefficients for cerium in the same temperature range did not vary significantly for concentrations ranging from 0.04 per cent to 0.6 per cent cerium. The rare-earth elements and barium were highly distributed into the calcium phase with distribution coefficients of around 10 or more (Table IV-6). As we expected, most of the cesium and a considerable amount of the strontium were volatilized. Less than 2 per cent of the barium was lost by volatilization, a figure comparable with that for calcium (about 0.3 per cent).

The uranium and uranium-plutonium alloys which have been melted under calcium (in an argon atmosphere) have been extremely clean due to the reducing properties of the calcium metal. The major problems are development of suitable container materials (tantalum has a maximum useful life of 5 hr and most ceramic materials are attacked) and the fact that fairly large volumes of calcium must be employed because of its relatively low density (~ 1.5) in order to realize high fission-product decontamination.

## Miscellaneous Pyrometallurgical Studies

A liquation process for separating ruthenium and molybdenum compounds from uranium alloys by a zone-melting type of treatment (repeated passage of molten alloy in one direction through a hot zone) is being investigated at the Bureau of Standards.[67]

A cyclic oxidation-reduction decontamination process is being investigated at Ames. The process involves dissolution of uranium in a $KCl-LiCl_2-ZnCl_2$ salt and successive reductions of impurities and uranium. At temperatures of 650°C uranium dissolved at a measurable rate, but for a practical dissolution rate the uranium must be finely divided.[71]

Studies on decontamination of thorium-uranium alloys by drossing reactions, volatilization by arc, and induction drip melting and by electrodeposition were recently reported by Brand et al.[58]

The thorium-uranium system has been studied over the range 0 to 20 wt.% uranium.[72] The

partial phase diagram for this range is shown in Fig. 14. The major conclusions are as follows:

1. The resistivity and lattice parameter data complete part of the thorium-uranium phase

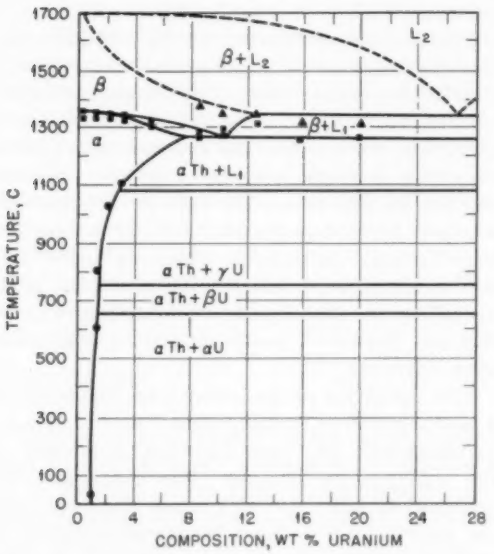


Fig. 14—Partial thorium-uranium phase diagram. ▲, alloy melted. ■, $\alpha$-$\beta$ transformation (resistivity data). ●, solubility (lattice parameter data). (Data taken from reference 72.)

diagram and confirm the following: (1) uranium causes a slight decrease in the $\alpha$-$\beta$ phase transformation temperature of thorium, (2) the solubility of uranium in thorium is less than 1 wt.% at room temperature and increases to about 7 wt.% at 1270°C, and (3) a $\beta + L_1$ region exists.

2. A study of the microstructures of the thorium-uranium alloys indicates that: (1) the uranium-rich phase occurs as a fine precipitate, evenly dispersed throughout the matrix in arc-melted alloys, (2) this precipitate agglomerates when the alloys are annealed, and (3) the uranium-rich phase is preferentially deposited in the grain boundaries.

3. The addition of 3 or more wt.% uranium strengthens thorium approximately 50 per cent at 500°C; considerable strengthening with increasing uranium was also noted at room temperature.

4. Apparently there is no correlation between the variations of tensile strength and the limits of solid solubility in the alloys studied.

## *Homogeneous Reactor Processing*

Homogeneous reactors are being studied at the present time at several locations, principally Oak Ridge, aqueous; BNL, bismuth-fueled; and Los Alamos, plutonium-fueled. A possible advantage of homogeneous reactors is the ability to remove a side stream continuously, process it to remove fission-product activity, and return it to the reactor. Efficiencies required of such processes need only be modest.

### Processing of Plutonium-enriched Fuels

Various techniques are being studied for the processing of the LAMPRE reactor fuel.[59,60] Six methods are being pursued: oxide slagging, molten metal extraction, oxidation by zinc chloride, liquation, mercury dissolution, and electrolysis.

In slagging experiments at 1400°C in a magnesia crucible, cerium and lanthanum were essentially removed in 8 hr. In similar experiments with zirconia crucibles, at temperatures of 1000°C using 10 per cent burn-up "fissium," no removal of cerium or lanthanum occurred in 4 hr. Fifty per cent of the lanthanum and 25 per cent of the cerium were removed at 1200°C in 4.5 hr. Raising the temperature to 1400°C improved the removal to 86 per cent for lanthanum and 39 per cent for cerium. Plutonium yields were 92 per cent at the higher temperature.

In molten metal extraction experiments, one volume of fissium melt was equilibrated with three volumes of calcium-magnesium eutectic. Lanthanum extraction was good, but zirconium, molybdenum, niobium, and ruthenium remained in the fissium phase. Little plutonium was extracted in a 24-hr contact, but after 48 hr the plutonium concentration in the extractant increased to 22 per cent. This is considered excessively high.

A 21-g ingot of plutonium-iron-fissium was dissolved in a 30 wt.% NaCl–70 wt.% $ZnCl_2$ mixture. The temperature used was 325 to 800°C. After the mixture was cooled to 500°C, the product salt was separated from the resulting zinc button. Good decontamination factors were obtained for iron, molybdenum, ruthenium, and zirconium, although no separation of lanthanum and cerium was attained. Plutonium losses to the zinc were 1.5 per cent.

Processing of plutonium-rich fuels by dissolution in mercury has been demonstrated on a small scale. Dissolution was complete in 5 hr at 330°C with a 10-g fuel button. Solubilities of lanthanum and cerium in mercury are being determined in the temperature range 20 to 300°C.

A plutonium-iron-fissium alloy has been electrorefined under an argon atmosphere in lithium chloride-potassium chloride eutectic bath containing 9 wt.% plutonium trichloride. The iron, ruthenium, zirconium, molybdenum, and niobium remained in the residual anode alloy. Cerium and most of the lanthanum accompanied the plutonium into the melt but were not redeposited. Cathode current efficiencies were 60 per cent. The prospects of this process appear excellent.

## Aqueous Homogeneous Reactors

A review of the activities of the past year in the Homogeneous Reactor Test (HRT) fuel and blanket processing facility has been reported.[9] In the initial reactor runs, high corrosion rates were observed. During this run an integrated power of 50 megawatt hours was achieved. The fuel was contaminated with corrosion product nickel. The second power run, in which the rated power of 5 Mw was achieved, was terminated by the sudden failure of the Zircaloy core tank.

Solids removed from the hydroclone system during the first radioactive run of 300 hr following the core rupture were analyzed and found to consist of 68 per cent $Fe_2O_3$, 7.5 per cent $Cr_2O_3$, 10.4 per cent $ZrO_2$, 2.5 per cent nickel, and 7.1 per cent aluminum. At the measured corrosion rate of 1 mil/year, about 1 kg of solids was produced in the core system during this period. This indicates that the hydroclone removed 10 per cent of the total solids. Solids content of the circulating streams was less than analytical or visual detection would allow but is estimated to be 1 to 2 ppm. The period of operation of the system was not long enough for the concentration of rare-earth group metals to reach their solubility limit. Hydroclone concentration factors of 330, 500, and 40 were achieved for zirconium, ruthenium, and tellurium.

Decontamination of the fuel can be done either by solvent-extraction procedures or by the precipitation of $UO_4$ with peroxide. Studies of the latter indicated that uranium losses will not exceed 0.2 per cent and that decontamination factors of >100 for nickel and >10 for neodymium, cerium, and cesium are achievable. Uranium losses can be minimized by controlling the uranium concentration in the solution, the pH near 3 and by using a low processing temperature, 2°C.

Fission and corrosion product solids were also studied in loops. One such loop containing a hydroclone operated for 3000 hr and collected 15 per cent of the iron and chromium oxide formed by corrosion. The accumulation of such materials in stagnant areas of the loop collected another 10 per cent. The balance is presumed to have formed a film 0.2 mil thick over the loop surface. In tests in which $Fe^{55}$, $Fe^{59}$, or $Zr^{95}$ tracers were added, $Zr^{95}$ deposited preferentially on Zircaloy-2, whereas the two iron isotopes deposited preferentially on stainless-steel surfaces.

The operation of the iodine trap consisting of a bed of silvered stainless-steel mesh has been satisfactory. The trap prevents poisoning of the catalytic recombiner. The charcoal traps designed to adsorb fission gases disposed from the reactor were tested by admitting bursts of $Kr^{85}$ into a flowing stream of oxygen, and the time for the activity to be discharged was noted. The test showed that there were no gross continuous void spaces in the four charcoal beds. Hold-up times for $Kr^{85}$ at a gas flow rate of 1 liter/min for each bed were 6 to 8 days. Extrapolation to reactor operating conditions indicate that krypton will be held in the beds for 23 days and xenon for 700 days.

One of the proposals to process the uranyl sulfate blanket was to retrieve the precipitated plutonium oxide with a hydroclone. However, laboratory and loop experiments have indicated that large percentages of the plutonium plates out on the internal parts of the equipment used. Similar results were obtained when circulating plutonium was well above solubility limits. Descaling of one experimental loop used for uranyl sulfate blanket processing studies indicated that 8 g of plutonium had been deposited in the loop. Three passes of chromous sulfate solution were used and successive passes produced 4.1, 3.7, and 0.9 g of plutonium, respectively.

Alternative processing methods for the uranyl sulfate blanket are being pursued. Selective adsorption on several inorganic solids shows

promise. These include $ZrO_2$, $Zr(OH)_4$, $Bi_2O_3$, and freshly precipitated $Ti(OH)_4$. Ion-exchange resin Dowex-50 also appears to be useful; however, radiation damage characteristics may eliminate this as a possibility.[9]

A topical report on the possibilities of ignition of the charcoal beds in the HRT has appeared. The ignition temperature of Columbia G activated charcoal in a flowing oxygen stream was determined to be 290°C under conditions simulating the inlet of the HRT charcoal beds. The calculation of the temperatures achieved in the charcoal beds due to fission-product heating of adsorbed fission gases indicate that the temperature of 290°C will not be exceeded unless the reactor power goes above 10 Mw with simultaneous increase in oxygen flow rate to 2 liters/min.[73]

## *Corrosion*

Corrosion is a subject which is an integral part of each process development. Because it is a problem which lends itself to setting up specific programs, however, much of the literature is reported under this specific heading. A variety of fuels are being proposed for use in newly contemplated power reactors. These cannot be directly accommodated in existing solvent-extraction facilities operated by the AEC. Head-end steps are being developed to adapt the processing of these fuels to the existing plants. Some of the processes require more than the usually corrosive chemicals.

### Solvent-extraction Processes

Darex is one of the processes proposed to dissolve stainless-steel matrix fuels. A pilot plant using titanium as the primary material of construction is being installed at Hanford. Titanium was selected over tantalum because it is less susceptible to hydrogen embrittlement.

The Niflex process is designed to dissolve stainless-steel clad fuels. In this system dissolution is accomplished with mixtures of nitric and hydrofluoric acids. Vacuum-melted Hastelloy F is considered the most promising construction material. Orders were recently placed for Hastelloy F components for construction of a pilot plant scale Niflex dissolver.[74]

The Zirflex process has been designed as a head-end treatment for zirconium fuels. Dissolving such fuels in ammonium fluoride solutions is one of two possible first steps in the process. In corrosion tests in which stainless steel type 304L was exposed to ammonium fluoride, the corrosion results were higher when conducted in teflon equipment as compared to glass. As a follow-up the tests were duplicated with additions of $SiO_2$, $B_2O_3$, $Cu_2(NO_3)_2$, and $Al(NO_3)_3$ in small quantities ($0.05M$ to $0.001M$). In each case corrosion was reduced to less than 2 mils/month under the most severe conditions expected. The inhibiting effect of copper nitrate was verified in alternate exposure tests made with stainless steel type 304L and Hastelloy F. The solutions used were boiling $6M$ $NH_4F-0.5M$ $NH_4NO_3$, and $10M$ $HNO_3$. The times were 8 and 16 hr, respectively; $0.01M$ $Cu(NO_3)_2$ was the additive in the former solution. The addition reduced the attack on the stainless steel from 12 mils/month to 2.4 mils/month. The corrosion in Hastelloy F decreased from 3.3 to 0.9 mils/month.[74]

The alternate first step of the Zircex process is vapor-phase hydrochlorination of the fuel at 600°C. A number of alloys were subjected to 75 11-hr periods in equimolar mixtures of anhydrous HCl and hydrogen. Cobalt-based alloys S-816 and S-590 suffered severe intergranular attack. Nickel, Illium R, and Hastelloy C showed no such effect. The latter appears to be the most promising at this time.

One of the proposed power reactor fuels consists of a thorium or thoria-bearing core clad with stainless steel. A possible processing method consists in decladding via Sulfex procedures (boiling $6M$ sulfuric acid followed by core dissolution in $13M$ $HNO_3-0.5M$ HF). It was reported in the preceding Review that Carpenter 20Cb was considered the most promising candidate as a material of construction. Recent tests indicate that this alloy may be susceptible to cracking in exposure to boiling $6M$ sulfuric acid. Heat-treating the alloy has not eliminated the effect. However, it has been noted that accumulated corrosion products in the solution will inhibit the cracking. Concentrations in excess of 1 g/liter are required.[75]

A number of other materials are being tested for use in the combination Sulfex-Thorex process. In cyclic tests ($4M$ and $6M$ $H_2SO_4$ initial and final Thorex dissolver solution) Nionel appeared to be about comparable to Carpenter 20Cb. However, serious intergranu-

lar attack has been observed in the heat-affected areas adjacent to welds. Illium R appears to be satisfactory in Thorex dissolver solutions provided additions of aluminum nitrate are made. Stainless steel type 329, Hastelloys C and F, Incoloy-804 and zirconium are also being studied. None of these withstand both Sulfex and Thorex conditions. Hastelloy C and zirconium have high corrosion rates in Thorex solutions, whereas the remaining have high rates of attack in Sulfex solutions.[75]

## Fused-salt Volatility Process

In this process zirconium matrix fuels are dissolved by hydrofluorinating in a fused fluoride medium; uranium hexafluoride is then recovered by fluorinating the dissolved uranium tetrafluoride. Both steps of this process have presented difficulties in the selection of a suitable material of construction. Molybdenum, silver, gold, and platinum were recently exposed to the dissolution environment: molten sodium fluoride–zirconium fluoride through which anhydrous hydrogen fluoride is bubbled at 600°C. Coupons were exposed simultaneously to the liquid phase, interface, and vapor phase. The corrosion on all metals tested was low compared to results obtained with nickel and nickel alloys. Partial experimental results are shown in Table IV-7.

Table IV-7 CORROSION OF SEVERAL METALS IN HYDROFLUORINATED SODIUM FLUORIDE–ZIRCONIUM FLUORIDE AT 600°C*

(Exposure: Coupons partially immersed in melt with hydrogen fluoride bubbled through melt alongside coupon)

| Metal | Exposure time, hr | Corrosion, mils/month: From weight loss | Corrosion, mils/month: Max. measured† |
|---|---|---|---|
| Mo | 445 | 0.1 | 0.2 |
| Ag | 667 | 0.03 | 0.3 |
| Au | 72 | 0.2 | 10 |
| Pt | 72 | 3 | 2 |

* Data taken from reference 76.
† Micrometer.

The same metals plus copper were exposed to the second step (fluorination) environment at 600°C. All were rapidly attacked at the interface. Hastelloy B was the only metal tested which showed some promise. In exposure to fluorine sparged melt for 21 hr plus helium for 34 hr the maximum dimensional change observed was 3.2 mils at the interface compared to 0.04 mil in the liquid phase and up to 1.8 mils in the vapor phase. Intergranular attack of 1.4 mils was observed in the vapor phase; none was observed at the interface or in the liquid phase.[76]

Table IV-8 PENETRATION OF TYPE CS GRAPHITE BY MOLTEN SODIUM FLUORIDE–ZIRCONIUM FLUORIDE UNDER PRESSURE AT 600°C*

| | |
|---|---|
| Crucible: | 6 in. O.D.; 3 in. I.D.; 11 in. height |
| Weight of melt: | 2250 g |
| $UF_4$ concentration: | 0.25 to 0.27 wt.% uranium |
| Helium pressure: | 1000 mm |
| Pretreatment: | 24 hr in uranium-free melt |

| Time, hr, at temp., with $UF_4$ | Distance from salt-graphite interface, mm | Salt concentration in graphite, wt.% | U content in salt, wt.% |
|---|---|---|---|
| 8 | 5.2 | 7.1 | 0.38 |
| | 16.9 | 6.4 | 0.22 |
| | 32.8 | 5.2 | 0.02 |
| 120 | 5.2 | 12.4 | 0.27 |
| | 10.6 | 11.0 | 0.25 |
| | 16.9 | 10.4 | 0.19 |
| | 24.6 | 6.5 | |

* Data taken from reference 76.
† Maximum if all voids filled: 32.5 wt.%.

Graphite is also considered a useful material of construction for the dissolution step of the process. Studies were made of the diffusion of uranium tetrafluoride into type CS graphite crucibles which had been pretreated by exposure to uranium-free sodium fluoride–zirconium fluoride for 24 hr. The content of uranium in the graphite was monitored after 8 and 120 hr to determine the diffusion characteristics. The results are shown in Table IV-8. Presaturation of the graphite with clean melt apparently does not adequately prevent uranium tetrafluoride diffusion into the graphite. The behavior of fission products in the melt would be expected not to differ markedly from that of uranium.[76]

The fused chloride extraction process for bismuth fuels uses a ternary eutectic of sodium chloride, potassium chloride, and magnesium chloride to which an oxidant, bismuth chloride, is added. In recent tests, SAE-1020 steel, alumina, magnesia, zirconia, and nitride-bonded silicon carbide were exposed to the ternary eutectic (no bismuth chloride). Magnesia cracked and spalled badly. Zirconia appeared

to be only slightly affected when bismuth chloride was present but showed some spalling in the plain eutectic. Alumina appeared to be superior. Nitride bonded silicon carbide appears to be satisfactory in the plain eutectic but spalls severely in the presence of bismuth chloride.[77]

Two topical reports have appeared recently on the corrosion of various alloys in liquid fluorine at temperatures[78,79] of −320°F.

## Pyrometallurgical Processing

One of the more challenging problems associated with pyrometallurgical processing is the metallic containment of molten uranium or uranium alloys. A borided tantalum crucible was tested in contact with molten uranium at 1250°C for 7 hr in a helium atmosphere. A clean looking ingot containing 500 ppm boron was removed from the crucible. Microscopic examinations showed no sign of erosion of the boride layer. An unborided crucible with a 25-mil wall was used as a control and was entirely corroded away under identical conditions.[4]

The corrosion of molten plutonium on various metallic construction materials is also of interest in pyrometallurgical processing. Tests continue in this environment for application in the LAMPRE reactor. The characteristic mode of attack on tantalum involves first an induction period when no mass transfer occurs, followed by a period of linear attack lasting until one of the components is exhausted. The rate of attack appears to be reproducible, but the length of the induction period is not. The test temperature is not given in the report. Typical results are shown in Table IV-9.

Table IV-9 CORROSION OF MOLTEN PLUTONIUM AND ITS ALLOYS IN TANTALUM

| Molten alloy | Attack, mils/yr | Induction period, hr |
|---|---|---|
| Pu-Co | 22 | 10–80 |
| Pu-Ce-Co | 1.3 | 100–1000 |
| Pu-Fe | 8 | |
| Pu-Ni | No results obtained | |

In other tests tantalum-tungsten, tantalum-niobium, tungsten, niobium, and molybdenum are being exposed to molten plutonium-iron alloy, and efforts are being made to determine the effect of impurities in the tantalum on its corrosion resistance. In rocking furnaces the corrosion was accelerated by increasing the temperature to 800°C. Niobium and molybdenum dissolved completely while tungsten was attacked slightly. It appears at the present time as though molten nickel-plutonium eutectic is the least corrosive fuel to tantalum.

## Miscellaneous Aqueous Corrosion

Corrosion studies are being conducted on type 316L and other 18-8 stainless steels immersed in STR processing wastes. The tests are conducted by inserting coupons of the metal under test into 30,000-gal type 316 stainless-steel storage vessels. Total exposure of specimens was 13 months: 11 months in zirconium fuel wastes, and 2 months in a composite zirconium fuel-Zircaloy fuel waste. The temperature was 25°C. Maximum corrosion observed was 0.011 mil/month. In a highly stressed and sensitized specimen, 15-mil pits were observed in a weld deposit.[80]

Head-end and waste evaporators at the ICPP used in uranium-aluminum fuel recovery are being redesigned in order to increase their capacity. New materials are also being studied for the application. A prototype titanium 75A evaporator was placed in service and corrosion measurements made after operation for six months at 137°C. Aluminum concentrations were 1.5*M* to 2.3*M*; nitrate, 5.6*M* to 8.4*M*; and acid, 1.1*M* to 1.3*M*. Corrosion was less than 0.01 mil/month, and no intergranular attack was observed. The titanium was also exposed to decontaminating procedures that are normally used on stainless steels. The corrosion observed was less than 16 mils/month.[80]

Mild steel is being tested in caustic-neutralized aluminum nitrate wastes. This method is an alternate to storing the acidic solutions in stainless-steel tanks. After exposure for 90 days vapor phase and interface specimens showed general pitting 10 to 15 mils deep. No liquid-phase corrosion was observed. Uniform corrosion was on the order of 1 mil/year.[80]

A topical report has been issued on the corrosion of materials by solutions containing nitric hydrofluoric acid mixtures and reducing agents. The reference acid concentration used in this study was 1.9*M* nitric acid and 1.1*M* hydrofluoric acid. All test temperatures were ambient. Type 309 Cb stainless steel corrodes

in the reference solution at 2.5 mils/year. Addition of 0.16*M* hydroxylamine nitrate or 0.11*M* sulfamic acid or both increased this reference rate by a factor of 160. Ascorbic acid had no influence. Additions of aluminum to complex the fluoride reduced the attack substantially. Ferric, cupric, and silver ions were much more effective in their inhibition requiring concentrations of 0.01*M*, 0.004*M*, and 0.001*M*, respectively, to achieve adequate corrosion rates. Other useful materials in this environment are silver, Hastelloy C, and Monel. Hastelloy C is preferred because of lower cost, superior mechanical properties, and better ability to withstand oxidizing agents.[81]

Several steels and titanium have been tested recently in Purex 2WW (second cycle aqueous waste) solutions at boiling temperatures. The rate of attack on sensitized stainless steels type 347, 304L, and 312 varied from 30 to 60 mils/year, whereas annealed A-70 titanium corroded at 3 mils/year.[82]

## *Instrumentation and Equipment Development*

A new filter that permits discharge of the filter cake and the reforming of a new cake remotely has been developed.[83] It is a magnetic filter in which the filter bed is a layer of ferromagnetic powder held midway in a column by means of a magnetic field generated across this area. The field is produced by an electromagnet, the opposite pole pieces of which surround the column. The filter may be built up by introducing the powder to the column while the current to the magnet is on. As the powder falls down the column, it is caught and held by the resulting magnetic field. Additional structural support is given to the bed by a stainless-steel screen across the column. Filtration, using the powder as the filter bed, may then be carried out in a conventional manner, the feed entering at the top, and the resulting filtrate passing out the bottom. After the filtration the old bed and filter cake may be discharged by simply turning off the current to the magnet and flushing the bed out the bottom with water or another liquid. This unit is more adaptable to an application where the filtrate is the product rather than the cake. The cake and bed can then be disposed of together without any subsequent separation.

Experimental work has been done mainly with ferrosilicon and type 431 stainless-steel powders. In a 4½-day exposure to 6*N* nitric acid at room temperature, ferrosilicon powder lost 0.2 wt.%. In a typical run the pressure drop across a 1.75-in. bed of 100-mesh ferrosilicon powder was 30 psi for 2 gpm flow rate in a 3-in. column.

An instrument has been designed to measure velocity and direction of flow of water in a large tank in which the flow was known to be nonuniform and three-dimensional.[84] The maximum dimension of the velocity-sensing element is limited to about 1 in. The instrument is capable of measuring the magnitude and direction of local velocities between 0.1 and 5 ft/sec. The direction and magnitude of the velocity vector in any two coordinate planes are measured within ±15 deg and ±0.2 ft/sec, respectively. The sensitive elements are thermistors connected in an anemometer type Wheatstone bridge feeding a recording instrument. The thermistors are installed in a tube with hemispherical ends with entrance and exit orifices so oriented to permit accurate determination of flow direction. The paper describes difficulties encountered and the method of calibration.

A special adaptation of the widely used variable area flow meter has been developed[85] for use at high pressures and with particularly hazardous fluids. The position of the float is sensed by absorption (by the float) of a beam of collimated gamma rays.

An eddy current method has been developed[86] to measure the depth of molten sodium or NaK in dump tanks 6 and 3 in. deep, with an accuracy of ±5 per cent.

A radioactive tracer method for measuring fluid flow was described for Geneva by Hull and Macomber.[87] The usefulness of the method has been shown over a wide range of flow rates varying by a factor of $10^9$. This technique has been used to measure a slow leak through capillary tubing, sanitary sewerage and storm run-off through sewers, exhaust gas from automobiles, and high pressure gas from a petroleum cracking plant.

Three in-line waste stream monitors were described at Geneva[88] which permit rapid accurate evaluation of levels and kinds of iso-

topes discharged to the environs. A total beta monitor consists of an automatic pipetter delivering a small sample into a depression on a moving aluminum tape. The sample is dried and counted automatically. A waste stream automatic analyzer was developed in which a more complex instrument automatically records the concentrations of seven isotopes which are predominant in a reactor coolant effluent. A gaseous waste analyzer-computer was developed to measure $Ru^{103}$, $Ru^{106}$, and $I^{131}$. A sample of potentially contaminated air is drawn first through a moving strip filter then through a packed column through which 0.2*N* sodium hydroxide flows continuously. Appropriate detectors measure and record the isotopes appearing in the scrubber solution and on the filter.

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*Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, September 1958. (Available from the Office of Technical Services, Dept. of Commerce, Washington 25, D. C.)

## General Surveys

The Second Geneva Conference produced a number of survey papers in the field of waste disposal. The experience at Hanford on the storage of wastes over a number of years was described by Pilkey et al.[1] At present and for many years in the future, the storage of radioactive waste liquids underground in metal containers is considered to be an economical and safe method. Storage in tanks has a number of limitations, however, including finite capacity, uncertain durability, vulnerability to accidents, and significant costs. The secure containment of liquid wastes at relatively high temperature for the necessary hundreds of years cannot be claimed as a method with absolute assurance against failure. The ultimate usable life of tanks is unknown. Although tank storage is considered an interim method of waste disposal, the technique in the present stage of knowledge has the advantage that the wastes are securely under control, their location is known, and experience to date has been satisfactory.

In order to minimize the duration of boiling and to recover certain long-lived fission products such as $Sr^{90}$ for anticipated large-scale uses, a large fraction of this isotope may be removed prior to storage. The safe storage period for waste liquids may thereby be extended since the waste would exist at a lower temperature and presumably under less severe corrosion conditions. Such a development depends on the realization of a continuing, large-scale demand for the long-lived fission products ($Sr^{90}$ and $Cs^{137}$) which may not occur soon. Furthermore, the problem of storage of the recovered isotopes is still at hand. The addition of any steps to the waste confinement process can be expected to be far more expensive than the existing cheap method of tank storage. Any such cost increase must be justified on the basis of real improvement in the problem of ultimate storage.

Future objectives directed at the solution of the problem are expected to be along the lines of processes which will convert liquid wastes into inert solids by some calcination technique. (See pp. 41 through 44.) The inert solids might then be packaged for permanent storage in dry vaults, pits, caves, abandoned mines, etc. (See pp. 45 through 48.)

Brown et al.[2] surveyed the experience in ground disposal at three major production sites.

Twelve years of practical experience in the controlled disposal of wastes to the ground at the Hanford Works, seven years at Oak Ridge National Laboratory, and four at the Savannah River Plant, have demonstrated the feasibility, safety, and economy in the disposal of at least limited volumes of some types of liquid wastes at shallow depths. The total volume and activity which have been disposed to ground at the three sites is shown in Table V-1. In addition to the $1.2 \times 10^{10}$ liters of radioactive wastes discharged to ground, Hanford has also discharged more than $1.0 \times 10^{11}$ liters of uncontaminated process cooling water to open swamps. The Hanford problem is one of management of large volumes of water as well as the control of the radioactivity. Within the limit of present experience and knowledge, demonstrable hazards have not developed at any of the three sites.

Table V-1 GROUND DISPOSAL AT THREE MAJOR U. S. PRODUCTION SITES*

| | Cumulative total volume, liters | Cumulative total gross beta-emitter activity, curies |
|---|---|---|
| Savannah River | $5.0 \times 10^8$ | $2.4 \times 10^2$ † |
| Oak Ridge | $2.6 \times 10^7$ | $1.0 \times 10^5$ |
| Hanford | $1.2 \times 10^{10}$ | $2.4 \times 10^6$ |

*Data taken from reference 2.
†Not including 2300 curies of $I^{131}$.

The French[3] gave design (but not operating) data for the waste disposal system at their production plant at Marcoule. The daily flow is 150 to 200 $m^3$ containing less than 1.5 curie/$m^3$. The process selected was one using coprecipitation and chemical coagulation. The reagents used

are monosodium phosphate, tannin, and sodium sulfate plus organic coagulation additive. Coagulation takes place in the presence of lime at a pH of about 11.5.

The decontamination factor expected ranges from 10 to 100. Processing equipment includes mixing vats and settling tanks which are installed in shielded cells. The hot residues are extracted as liquid muds which contain approximately 2 per cent solids. The muds are filtered, producing thick muds (60 to 70 per cent water). These wastes are kept in galvanized sheet metal barrels, 255-liter capacity and lined with polyethylene. The intensity of gamma radiation of a full barrel reaches 30 to 40 r/hr. The full barrels are taken out with the help of a shielded truck and are stored in a protected area. This is considered provisional, and an ultimate storage has not been selected.

In July 1957 the Fifth Atomic Energy Commission Air Cleaning Conference was held at Harvard University. The record of that conference is now available.[4] In addition to covering general work at each of the sites on air cleaning, problems associated with the start-up of the Argonne Experimental Boiling Water Reactor (EBWR), developments in high efficiency filters and fire resistant filters, and economic data are presented.

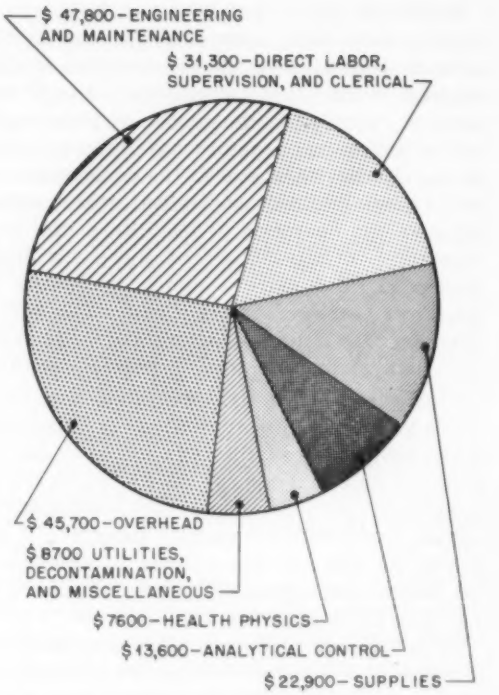
$ 47,800 – ENGINEERING AND MAINTENANCE
$ 31,300 – DIRECT LABOR, SUPERVISION, AND CLERICAL
$ 45,700 – OVERHEAD
$ 8700 UTILITIES, DECONTAMINATION, AND MISCELLANEOUS
$ 7600 – HEALTH PHYSICS
$ 13,600 – ANALYTICAL CONTROL
$ 22,900 – SUPPLIES

Fig. 15 — Waste-disposal costs at ORNL for 1957. (Data taken from reference 5.)

## *Operating Experience*

Oak Ridge National Laboratory (ORNL) reports[5] that the total operating cost of their radioactive waste-disposal system in 1957 was $177,600. A breakdown of these costs is shown in Fig. 15. Cowser et al.[6] described in a Geneva paper a lime-soda process plant used as an adjunct to the ORNL waste-treatment system. Designed especially for the removal of strontium, the plant has shown reductions of 80 to 90 per cent of the radioactivity due to strontium in the wastes that have been treated. The other radionuclides that have a significant though less dominant influence on the MPC values for water can be reduced 50 to 90 per cent or more.

At Hanford, a gamma-ray spectrometric system of analysis, which requires no chemical separations, has been developed for the measurement of $Na^{24}$, $Sc^{46}$, $Cr^{51}$, $Mn^{54}$, $Mn^{56}$, $Co^{60}$, $Cu^{64}$, $Zn^{65}$, $Ba^{140}$, and $Np^{239}$, in reactor effluent water.[7] The isotope, $As^{76}$, can also be measured spectrometrically; however, the precision of its measurement is less than that obtained by a beta-ray absorption technique. The analyses are based on a combination of gamma-ray and coincidence gamma-ray spectrometric techniques. The measurements are all made on the residue from the evaporation of a reactor effluent water sample. The analyses require very little analytical time and are an attractive substitute for the "wet chemical" procedures which they have replaced. The applicability of these procedures for routine use was demonstrated by analyzing the effluents from each reactor daily for a one month period with a single channel analyzer.

A study[8] is being directed toward discovery of the sources of some of the radioisotopes in reactor effluent water. Preliminary results show that parent isotopes for $P^{32}$ and $As^{76}$ are present in the process water largely from contaminants in the river not removed in the water treatment process.

Hanford experience with the treatment of radioactive gaseous wastes was described at Geneva by Blasewitz and Schmidt.[9]

Fixed-bed glass fiber filters and the silver reactor have been adopted at Hanford as the methods best meeting the requirements for the efficient removal of radioactive aerosols and gaseous radioiodine. A number of plant-scale filters and silver reactors have been operated during the past eight years. The performance of both types of equipment has been highly satisfactory. The operation of the filters has been essentially maintenance-free and particularly uneventful. The more complex mechanism of the silver reactor requires considerably closer attention. The following factors are particularly important in the operation of silver reactors.

1. If the reactors are permitted to operate below 375°F, the collection efficiency is lowered; if the temperature falls below the condensation point of nitric acid vapors (230°F), practically no iodine removal occurs. If a reactor using silver nitrate is permitted to operate above 413°F, the life of the unit will be seriously affected due to the melting and flowing of the silver nitrate coating from the column packing.

2. Either stable iodine or chlorine can saturate a reactor or displace radioactive iodine which has been collected. For this reason, care should be exercised that the chemicals used in the process do not contain appreciable amounts of chlorine or iodine.

There has been one instance of an explosion in a silver nitrate reactor. This incident is described on p. 3 of this Review.

Additional studies on the silver reactors[10] have shown that controlling the temperature of influent gas to the silver reactors at 250°F during aluminum jacket removal had no apparent effect on the efficiency of iodine removal, but did result in marked increases in the temperature of reactor effluent gases of anywhere from 30 to 130°F. This was attributed to the highly exothermic reactions occurring between ammonia and silver nitrate.

When jacket removals were followed by uranium dissolving during which the silver reactor influent temperature was controlled at 395°F, the reactor effluent gas temperature rose by from 40 to 150°F.

The large temperature increases across the silver reactors observed in the course of these tests indicate that the silver nitrate is in the molten state for several hours during both jacket removal and uranium dissolving. This provides a very strong argument for bypassing the silver reactors during coating removal to increase the life expectancy of the reactors.

A fundamental study of the reaction of iodine with silver nitrate has been reported.[11] Throughout the temperature range investigated, which included the operating temperature of 200°C, the diffusional process through the gas film was very rapid relative to the chemical reaction rate at the surface.

The rate of reaction was found to increase slightly with temperature, while varying the flow rate at a constant temperature produced almost no change in reaction rate. The reaction velocity constant, k, was determined at various temperatures and an activation energy of 158 calories per gram molecule was determined. Because of this low value, the rate-controlling mechanism was postulated to be one of diffusion of the adsorbed iodine through the molecular films of silver iodide first formed to the reacting silver nitrate underneath.

## *Volume Reduction*

Work was reported from two sites on the destruction of nitric acid in waste streams by formaldehyde. The 3*N* nitric acid in a simulated Darex solution was destroyed by formaldehyde at 90°C in 5 hr with the final pH of the solution being 2.5. The nitrate was reduced from 314 g/liter to 17 g/liter. Another portion of the Darex waste was made 3*N* in sulfuric acid for a total acidity of 6*N* and the nitric acid again destroyed by formaldehyde at 90°C. The pH of the final solution, after 3 hr, was 1 and the nitrate was reduced from 314 g/liter to 0.7 g/liter.

Hanford has nearly completed construction of a pilot plant unit for the formaldehyde destruction of nitric acid.[12] The primary reaction vessels (a 4-gal stainless-steel pot and surmounted absorption tower) of the pilot plant will be housed in an empty 30,000-gal underground storage tank to confine the reaction products in the event that excessive pressures are developed during exploratory studies.

Laboratory experiments on the electrolytic destruction of nitric acid (to NO and $NO_2$) were continued.[13] In a two-compartment cell using a Permutit 3142 cation membrane, a stainless-steel cathode, and a Duriron anode, current efficiencies ranged from 90 per cent (2.1 g nitric acid/amp-hr) with 8*M* nitric acid to

50 per cent (1.2 g nitric acid/amp-hr) with 4*M* nitric acid.

In a batch electrolysis of synthetic Purex first cycle waste, 88 per cent of the free nitric acid was destroyed at an over-all current efficiency of 57 per cent with a stainless-steel cathode, no diaphragm, and a Duriron anode. The cell voltage was 5.0 volts at a current density of 1.5 amp/sq in. During the course of the electrolysis, the solution volume decreased by a factor of 3. Although electrode corrosion rates were not measured, other tests with nitric acid as electrolyte have given corrosion rates of about 25 and 4 mg/(amp)(hr) for the anode and cathode, respectively.

## *Reduction to Solids*

Work is reported on the adsorption of activity onto clays, minerals, and glasses and on several methods of calcining waste solutions. Work on the *in situ* retention of wastes in soils is covered on pp. 45 through 48.

### Adsorption of Activity on Natural Materials

The capacity of a 50-g bed of crushed calcite for removing $Sr^{90}$ from 0.05*M* phosphate solutions is being tested. The test bed is continuing to receive solutions containing $3.2 \times 10^{-2}$ μc/cc of $Sr^{90}$ with no apparent breakthrough of radiostrontium after passage of 1500 column volumes of solution. The test column is providing solution decontamination factors ranging from $10^5$ to $10^6$. Other carbonate minerals were tested and found to remove strontium from alkaline phosphate solutions in the same manner as calcite. Those tested include siderite ($FeCO_3$), smithsonite ($ZnCO_3$), and rhodochrosite ($MnCO_3$).

The use of Krilium and gelatin as additives has increased considerably the stability of extruded clay to immersion in water. In a leaching study of calcined oxides of aluminum and zirconium, leaching at 90°C resulted in no increase in amounts of cesium and strontium removed from the oxide matrices as compared with the values obtained at room temperature.[14]

The process under study at Chalk River for inclusion in a glass, nepheline syenite, was described for the Geneva meeting by Watson et al.[15]

Nephelene syenite melts at about 1250°C and when cooled forms a glass. When an acid solution is mixed with nepheline syenite, the nepheline is attacked and produces a silica gel. Such a gelled mix may be dried rapidly without serious entrainment of particulate material during the removal of water, nitric acid, oxides of nitrogen, and other volatile compounds. A flow sheet by which fission products may be incorporated into glass blocks is presented in Fig. 16.

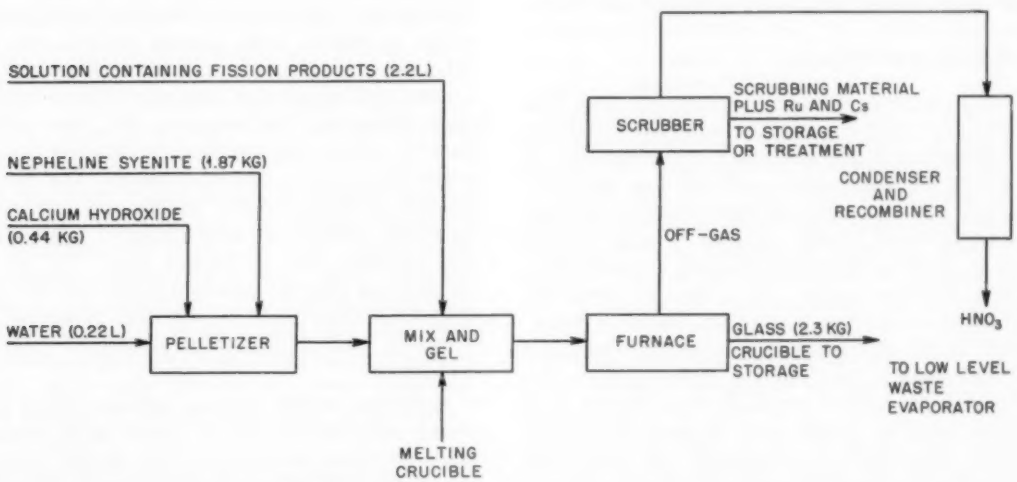


Fig. 16 — Flow sheet for incorporation of fission products into nepheline syenite. Quantities indicated are those required to fill one 4.5 liter crucible at the mixing stage. (Data taken from reference 15.)

It has been shown earlier that the rate of leaching of activity from nepheline syenite glass by immersion in water is very low; a conservative figure corresponds to the dissolution of $3 \times 10^{-7}$ g of glass per square centimeter per day.

If the fission products produced by reactors having a total capacity of 4000 thermal megawatts were incorporated into glass leaching at $3 \times 10^{-7}$ (sq cm)(day), the cumulative figures for radionuclides leached from the glass would be as set out in Table V-2.

Table V-2 CUMULATIVE LEACHED ACTIVITY FROM NEPHELINE SYENITE GLASS CONTAINING FISSION PRODUCTS PRODUCED CONTINUOUSLY AT A CONSTANT RATE*

| Nuclide† | Cumulative leached material, curies | | |
|---|---|---|---|
| | 1 year | 5 years | 25 years |
| $Sr^{90}$‡ | 15.2 | 290 | 6460 |
| $Ru^{106}$ | 30.5 | 399 | 400 |
| $Cs^{137}$ | 22.6 | 566 | 9670 |
| $Ce^{144}$ | 73.3 | 537 | 540 |

*From 4000 thermal megawatts of installed reactor capacity.

†Daughter activities are not included.

‡The quantity of $Sr^{90}$ in the stored glass after five years would be $1.3 \times 10^7$ curies.

A rough cost estimate of this process indicates that it should contribute not more than 0.05 mill/kw-hr to the cost of power. (The fuel was assumed to have a burn-up of 10,000 Mwd/ton.)

## Calcination of Wastes

At a number of sites methods for removing water from wastes and at the same time calcining the resulting solids are under consideration. At Hanford an 8-in. spray calciner has been designed, and experimental data are being obtained on an agitated trough calciner,[12] using as fuel (1) an acid-killed (formaldehyde treated) first cycle aqueous waste, (2) a similar feed with phosphate and borate addition, and (3) a simulated ICPP aluminum nitrate waste. The effect of calcination time on the volatilization and leaching of fission products from Purex first cycle aqueous waste was studied at 400 and 800°C. The fraction volatilized did not change markedly for heating times ranging from 5 min to 24 hr. For 400°C calcination, the leachability of the residue was also not affected, but at 800°C the leachability decreased greatly — from 73 per cent leached after 5 min heating to only 3 per cent after 24 hr. Other experiments showed that higher temperatures, 1000 and 1400°C, resulted in low fission-product leachability independent of the initial composition of the waste. However, volatilization of sodium salts and cesium was evident at the higher temperature.

The fluid-bed calcining program at Argonne and Idaho Chemical Processing Plant was described at Geneva.[16] The AEC announced on Oct. 9, 1958, that construction of a 60-gal/hr demonstration pilot plant for this process had begun at Idaho. This facility is designed to develop engineering information and will be capable of calcining wastes generated from processing fuels at 200 days post reactor discharge. The basic components of the process are (1) the calciner and its auxiliaries, (2) off-gas treating equipment, and (3) solids storage facilities.

The fluidized-bed calciner is designed to operate under a slight negative pressure and a temperature of 400 to 500°C. Calcined alumina will be pneumatically transported to the solids storage bins by an air stream which will be returned as part of the fluidizing air. Local air tolerance levels are such that the nitrogen oxides can be discharged to the atmosphere provided they are within the tolerance limits on radioactivity. A simple but highly efficient off-gas system will be required to avoid emission of radioactive particulates to the environment. Therefore, the system chosen for the preliminary design consists of several air cleaning devices in series. Upon leaving the calciner the off-gases will pass through high-efficiency cyclones, wet scrubbers, adsorber-filters packed with silica gel, and absolute AEC type filters before joining the building ventilation air for stack discharge to the atmosphere. The system chosen is mechanically simple and involves a minimum amount of remote removal equipment. For example, the silica-gel beds will be incorporated with the calcined solids for storage. The final filters will be the only remotely removable and replaceable pieces of process equipment.

Sufficient solids storage volume will be provided with the facility to store three hundred days of plant production. The design criteria for the solids storage system was to limit the center line temperature to a value not exceeding the calcining temperature of 400°C. This temperature was chosen on the assumption that

Table V-3 PERFORMANCE OF WASTE CALCINER OFF-GAS SYSTEM

(Run time: 6 hr)

| Temp., °C | Dilution of ICPP waste | Feed activity, counts/min | | Decontamination factors, avg. | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Ruthenium | | | | Nonvolatile fission products | | | |
| | | Gross γ | Ruthenium γ | Across calciner | Across scrubber | Across adsorber | Over-all | Across calciner | Across scrubber | Across adsorber | Over-all |
| 400 | 250:1 | $1.18 \times 10^6$ | $4.96 \times 10^4$ | 1.05 | 1.8 | 350 | $6.60 \times 10^2$ | 390 | 1.06 | 81 | $3.2 \times 10^4$ |
| 500 | 250:1 | $1.13 \times 10^6$ | $4.70 \times 10^4$ | 3.8 | † | 2900 | $1.09 \times 10^4$ | 114 | 3.7 | 340 | $1.4 \times 10^5$ |
| 400 | 90:1 | $3.00 \times 10^6$ | $1.25 \times 10^5$ | 1.05 | 1.4 | 4200 | $6.20 \times 10^3$ | 114 | 3.7 | 340 | $1.4 \times 10^5$ |
| 500 | 90:1 | $3.00 \times 10^6$ | $1.25 \times 10^5$ | 3.3 | † | 390 | $1.30 \times 10^3$ | 156 | 3.7 | 135 | $5.5 \times 10^4$ |
| 400* | 100:1 | $2.90 \times 10^6$ | $1.09 \times 10^5$ | 1.05 | 1.3 | 700 | $1.00 \times 10^3$ | 52 | 10.0 | 101 | $5.3 \times 10^4$ |

*Eighty-five hour run.
†No contamination detectable.

fission products not volatilized in the calciner would not be volatilized in the storage bins. Based on these criteria a design employing forced air cooling of storage bins has been adopted. The solids will be contained in narrow vertical annular chambers with intervening air cooling passages. A large number of temperature measuring points will be installed since the design is sufficiently flexible to determine if temperatures above 400°C can be tolerated without creating an off-gas problem.

Certain components of the proposed off-gas system have been tested at Argonne using diluted ICPP active waste. The results[17] of five recent runs are shown in Table V-3. At a calcination temperature of 400°C a ruthenium decontamination factor across the calciner, scrubber, and adsorber of about $10^3$ has been obtained. At 500°C these ruthenium decontamination factors have been in excess of $10^4$ for the best runs. Nonvolatile fission products have been removed by factors of greater than $10^4$. The results are approaching satisfactory limits.

Laboratory experiments at Idaho demonstrated that less than 1 per cent of the ruthenium that was adsorbed on a silica-gel column from the off-gas during calcination, was eluted by washing the silica gel with carbon tetrachloride.[18] These data suggest that the ruthenium tetroxide, which was volatilized from the calciner, was totally reduced to a lower oxidation state prior to or during adsorption in the silica-gel column.

Samples of calcined alumina containing $Ce^{137}$ spike were heated in a quartz combination tube, and the volatile products were collected in the "cold end" of the combustion tube and in a liquid scrubber. Analysis of the scrubber solution, combustion tube washings, and alumina after heating for approximately 40 hr at 800 to 1200°C indicated that the amount of cesium volatilized ranged from about 10 per cent at the lower temperatures to approximately 80 per cent at the higher temperatures. The material balances were usually between 90 and 100 per cent.

## *Removal of Specific Isotopes*

In a Geneva paper, Moore and Burns[19] gave a good statement of the relationship of fission-product recovery and waste disposal. They record the historical identification of fission-product recovery with waste disposal and the argument that, if strontium and cesium are removed, the remainder can, after a few years of storage, be relatively easily disposed (see, e.g., Gluekauf, First Geneva Conference).

Separations process effluents currently available for large-scale fission-product recovery contain $Ce^{137}$ and $Sr^{90}$ in concentrations of between $10^3$ and $10^4$ μc/ml. To reduce these nuclides to drinking water tolerances, minimum decontamination factors of about $10^6$ and $10^9$, respectively, would be required. Suggested recovery processes give decontamination factors ranging from only about 10 to 100. This is due to the necessity of keeping the process simple and producing a product of high specific activity. Economically competitive processes giving decontamination factors of $10^3$ may possibly be devised, but it appears highly improbable that competitive processes giving decontamination factors of $10^6$ to $10^9$ can be developed. Effluents from presently suggested cesium and

strontium recovery processes will contain many times drinking water tolerances for $Ce^{137}$ and $Sr.^{90}$ Thus, even though these effluents are stored until all short-lived nuclides have decayed to sub-hazardous levels, they still cannot be safely discharged where they might contaminate public waters.

There are undeniable fringe benefits to waste disposal resulting from fission-product recovery. The magnitude of the catastrophe should a waste storage tank rupture would certainly be diminished if most of the cesium and strontium had been removed. In long-term storage or ultimate disposal techniques in which decay heat is a problem, prior removal of $Ce^{137}$ and $Sr^{90}$ will reduce the problem. But while recovery of specific fission products from process effluents may reduce heating problems in long term retention of radioactive wastes, it appears unlikely that the very high $Ce^{137}$ and $Sr^{90}$ decontamination factors required to permit eventual uncontrolled release of the wastes will be obtained in economically competitive recovery programs.

Two United Kingdom papers prepared for Geneva described the recovery of actinide elements from waste streams[20] and the recovery of $Kr^{85}$ from dissolver off-gases.[21]

The French reported that a hot laboratory building 14 by 10 meters has been installed for the extraction of $Ce^{137}$ from fission-product solutions containing 100 curies/liter.[22] The process used consists in precipitation of cesium as phosphotungstate, washing of the cesium in ammonium phosphotungstate, decomposition of the precipitated salt by baryta, elimination of the ammonia, and elimination of the barium. Cesium sulfate solution is then concentrated and evaporated until dry. The final product contains about 5 wt.% barium sulfate.

In September the AEC announced that the multicurie fission-product pilot plant at the ORNL had started operations.[23] The 2.2 million dollar plant will separate industrially usable isotopes in kilocurie quantities from the radioactive wastes from ORNL and other AEC facilities. The principal isotopes processed will be $Ce^{137}$, $Pm^{147}$, $Sr^{90}$, $Cm^{144}$, and $Tc^{99}$.

## *Final Disposal Methods*

In this section work is reported on methods for "final" disposal of wastes with or without ultimate control of the activity. This quarter information is available on disposal to ground at shallow depths and to the ocean. In addition the storage of activity in asphalt-lined pits and in salt formations is discussed.

Hanford, which possesses one of the most favorable geological situations for ground disposal, has long been interested in, and has used, the method of disposal to ground. The term "specific retention" is used a good deal in reports on this subject and its meaning is somewhat confusing because of conflicting definitions applied by the several geosciences. As used at Hanford the term may be defined as the volume of water that may be disposed to the soil and be held against the force of gravity by the surface tension characteristic of the soil surfaces and pores, when expressed as per cent of packed soil volume.[24] In practice it represents the volume of liquid that may be discharged to a pit of known dimensions without leakage to the ground water, expressed as per cent of the total volume of a column of soil with the same cross section as the pit, and extending from the bottom of the pit to the water table. It is recognized that some degree of lateral spreading will occur which has the effect of enlarging the volume of soil contacted by the liquid. This is a benefit of unknown magnitude that is accepted as a safety factor.

A laboratory research study was initiated to study the movement of boiling, high-level Redox waste solutions through soil, simulating wastes which could leak from an underground tank.[8] The study is designed to determine the influence of salts crystallizing out of cooling synthetic waste solutions on the ability of the soils to transmit the solutions.

Two field-scale tests were performed to simulate loss of Redox waste through a leak in an underground storage tank. The first test used simulated neutralized Redox waste which had not undergone self-concentration. It contained a precipitate equal to about 5 vol.%. This waste entered the ground through a 1-in. hole in a 7-ft by 7-ft test plate without giving any indication of developing a flow restriction either by a waste-soil reaction or by the precipitate plugging the soil. The maximum flow recorded was 450 gal per hour. When the plate was removed, visual examination showed that the precipitate had dispersed in the soil, forming a saucer-shaped pattern about 2 ft deep in the center and with a radius of 7 ft. Analytical results substan-

tiated the visual observations and indicated that precipitate-free waste had penetrated to a depth of 4 ft in the center and had spread to about an 11-ft radius.

The second test employed synthetic solutions which simulated Redox waste self-concentrated to 83 per cent of its original volume. This waste contained about 20 vol.% of a rapidly-settling precipitate. Only 50 gal of this waste entered the ground before plugging occurred and all measurable flow stopped. The plugging was apparently due to the precipitate settling in the bottom of the stand-pipe. Visual examination of the soil beneath the place indicated that clear waste had spread to a radius of about 3 ft. A third test is planned.

The Oak Ridge experience with ground disposal was sumarized for the Geneva meeting by de Lagana et al.[25] The concept of the pit as a tank has been largely abandoned, for few if any earth materials are sufficiently impermeable. The three waste-disposal pits now in use at Oak Ridge are of value not for their storage capacity, but for the ability of the soil around them to trap and hold the radioactive constituents in the waste as it seeps out.

The pits have been operating for about seven years and have handled with apparent safety many millions of gallons of radioactive waste. There is some concern, however, about their future. It is unlikely that it will even be possible to determine in as much detail as desirable the movement of the radioactive materials away from pits of any type. In an area of more homogeneous rocks and simpler structure, it would be possible to learn more, but it does not appear that such a device can ever be operated safely near important centers of population if it is required to handle substantial amounts of radioactive materials. Disposal pits can serve a useful purpose, as they have at Oak Ridge, as a temporary measure to handle limited amounts of waste while better methods are being developed.

The sea, because of its size, has always had its appeal as a disposal medium. Disposal to the oceans also results in loss of ultimate control of the activity.

A report of the Committee on Atomic Radiation on Oceanography and Fisheries of the National Academy of Sciences has become available during the past quarter. This book[26] covers in some detail the physical and chemical properties of wastes produced, the comparison of some natural radiations received by selected organisms, fission-product spectrum in the sea as a function of time and mixing characteristics, transport and disposal of radioactive elements in the sea, the effect of ecology, precipitation of fission-product elements on the ocean bottom by various processes, and discussions of cumulation and retention of radioactivity by various organisms both fresh water and sea water.

Some of the oceanic research which would be needed for safe use of the sea as a disposal medium was presented for Geneva by Revelle and Schaefer.[27] In the last Review of this series[28] British data on discharge of wastes into the Irish Sea at Windscale were mentioned. Further data on this work were presented at Geneva by Dunster.[29] A summary of results of the Windscale surveys is given in Table V-4.

The results of this experimental program have shown that it would be safe to release some 20,000 curies per month of fission products at a point about 3 km off this part of the Cumberland coast. Further work now in hand suggests that this figure could reasonably be increased, possibly to as much as 100,000 curies per month. These high figures are possible because the marine processes in this area cause sufficient dispersal to prevent any continuing build-up from year to year in the activity levels, either in the vicinity of the outlet or in the more widespread regions of the Irish Sea.

Based on the Windscale experience, the British propose to use similar methods on the north coast of Scotland at Dounreay and on the south coast of England at Winfrith Heath. A paper describing the survey (using dye) of the latter area was prepared for Geneva by Bowles et al.[30] It is proposed to convey the effluent from the Winfrith Heath site to the coast by buried pipelines and thence out to sea. The results of these experiments combined with Windscale experience led to the conclusion that a regular discharge of 25,000 curies per month would be permissible off Arish Mell if the release point is 2 miles out to sea. In all probability the initial discharge will be in the order of $\frac{1}{10}$ of this amount.

The Russians also had something to say on the subject at Geneva.[31] Among the plans for the disposal of radiowaste, the suggestion that the waste packed in containers should be dumped into ocean trenches deserves attention. This project is based on the belief that the water in ocean trenches does not circulate either in a

Table V-4 SUMMARY OF RESULTS OF DISCHARGES FROM WINDSCALE*

| Type of activity and sample | Weighted mean activity for a discharge rate of 1 curie/28 days, $\mu\mu c/g$ | Maximum permissible level, $\mu\mu c/g$ | Fraction of mpl resulting from a discharge rate of 1 curie/28 days |
|---|---|---|---|
| Total alpha | | | |
| Seaweed | $3.1 \times 10^{-2}$ | 10 | $3.1 \times 10^{-3}$ |
| Fish | $4.1 \times 10^{-3}$ | 30 | $1.4 \times 10^{-4}$ |
| Mussels | $3.1 \times 10^{-1}$ | 30† | $1.0 \times 10^{-2}$ |
| Total beta | | | |
| Seaweed | $3.2 \times 10^{-2}$ | 670 | $4.8 \times 10^{-5}$ |
| Fish | $1.6 \times 10^{-3}$ | 2,000 | $8 \times 10^{-7}$ |
| Mussels | $8.2 \times 10^{-2}$ | 2,000† | $4.1 \times 10^{-5}$ |
| Shore sand | $1.3 \times 10^{-2}$ | 25,000 | $5.2 \times 10^{-7}$ |
| Shore silt | 2.0 | 100,000 | $2 \times 10^{-5}$ |
| Sea bed | $6.9 \times 10^{-1}$ | 100,000 | $6.9 \times 10^{-6}$ |
| Ruthenium-106 | | | |
| Seaweed | $4.1 \times 10^{-2}$ | 330 | $1.2 \times 10^{-4}$ |
| Fish | $1.0 \times 10^{-3}$ | 1,000 | $1.0 \times 10^{-6}$ |
| Mussels | $3.0 \times 10^{-2}$ | 1,000† | $3.0 \times 10^{-5}$ |
| Shore silt | 1.1 | 100,000 | $1.1 \times 10^{-5}$ |
| Sea bed | 1.3 | 100,000 | $1.3 \times 10^{-5}$ |
| Total beta (excluding $Ru^{106}$) | | | |
| Seaweed | $1.7 \times 10^{-2}$ | 670 | $2.5 \times 10^{-5}$ |
| Fish | $1.3 \times 10^{-3}$ | 2,000 | $6.5 \times 10^{-7}$ |
| Strontium-90 | | | |
| Seaweed | $9.7 \times 10^{-4}$ | 2.7 | $3.6 \times 10^{-4}$ |
| Fish | $6.3 \times 10^{-4}$ | 8 | $7.9 \times 10^{-5}$ |

*Data taken from reference 29.
†Same figure taken as for fish, although off this coast mussels are not used for food.

vertical or horizontal direction or that its circulation is so slow that radioactive waste dumped into it and dissolving there will not be carried out of the trench and pollute the ocean waters, and will not therefore contaminate the fish and other marine products of commerce. This viewpoint has already met objections from Soviet scientists.

There are nineteen deep-sea trenches in the world ocean with depths exceeding 7 km. Fifteen of them are in the Pacific, one in the Indian and three in the Atlantic ocean. The oceanographic investigations carried out by the "Vityaz" covered twelve of these trenches. The factual data obtained justify the contention that trenches are unsuitable places for the disposal of radioactive waste.

Turning consideration to methods of storage which maintain control of the activity some time ago the suggestion was made that wastes be stored in asphalt-lined pits.[32] Recent data[33] indicate that asphaltic membranes appear practical for lining earth storage pits for aqueous radiochemical waste provided that the wastes are neutralized and are decayed sufficiently that the self-heating temperature does not exceed 150°F and the time for the asphalt to acquire a dose of $10^9$ r is more than 25 years.

Calculations show that wastes from fuels irradiated to 10,000, 3300, and 1000 Mwd/ton and decayed six years would irradiate an asphalt lining to $10^9$ r in 20, 79, and 300 years, respectively; with 10 years of decay the times would be 27, 95, and 365 years. Longer decay

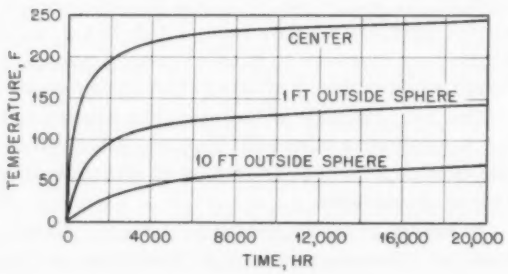


Fig. 17—Time-space temperature distribution of waste stored in salt cavities. Twenty-foot-diameter sphere; conduction only. (Data taken from reference 34.)

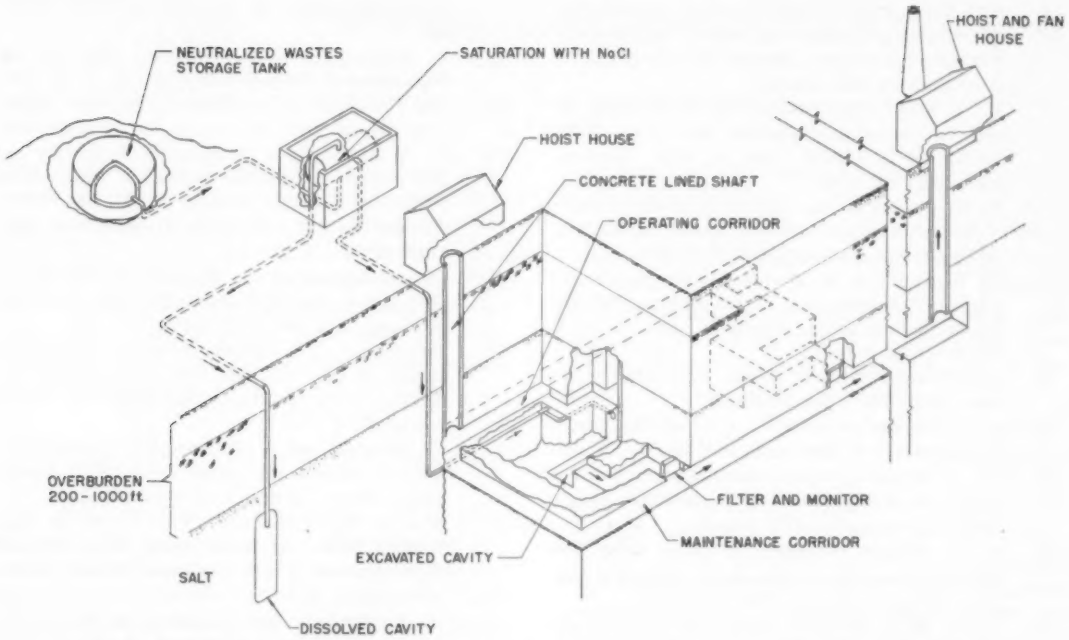


Fig. 18—Disposal of radioactive wastes in salt formations. (Data taken from reference 34.)

times offer little, if any, advantage. An open pit of $10^6$ gal capacity could be constructed for $0.03 per gal, and one with a concrete roof for $0.07 per gal; corresponding costs for a $5 \times 10^6$ gal pit would be $0.02 and $0.05 per gal.

One of the more promising methods of storage involves the use of natural salt formations. A program coordinated through ORNL is under way to determine the feasibility of using salt formations as an ultimate storage place for either liquid or solid wastes.[34] The seven-point research program includes heat calculations, chemical compatibility, physical stability of the system, design of a field experiment, test of laboratory model of field experiment, field experimental sites, site selection and procurement, and the field experiment itself.

The suggestion for the use of cavities and salt formations for the storage of radioactive wastes has been prompted by the knowledge that the petroleum industry has been storing liquefied petroleum gases economically and safely in salt formations since 1950. The growth and storage capacity for petroleum has been spectacular from 0 in 1950 to 7,000,000 barrels in 1952 and over 25,000,000 in early 1957.

Heat calculations have been made by Professors Schecter at Texas and by Birch at Harvard. Time-space temperature distributions based on limiting the temperature rise at the edge of a sphere to 200°C with waste producing 2 Btu/hr/gal are shown in Fig. 17. Studies of mechanical properties of salt are well under way under Gloyna at the University of Texas.

A preliminary conceptual design of what an operating facility in salt might look like is given in Fig. 18. Preliminary discussions are well under way to get a field experiment into operation. The initial test will use synthetic wastes and simulated heat sources followed by tests using waste containing tracer solution.

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The conversions of solutions of purified uranium, plutonium, and thorium salts into intermediates and then to metals and the reconversion of uranium hexafluoride into intermediates for metal or oxide production have been undergoing continual development and improvement over a period of years. New developments and descriptions of processes, plants, and techniques are reviewed herein.

## *Reduction of Uranium Hexafluoride*

A dry process for reduction of uranium hexafluoride to uranium tetrafluoride by reaction with hydrogen gas was described in the last Review.[1] In this process, called the "Cold Wall Process," the continuous addition of fluorine gas with the uranium hexafluoride feed stream supplied the heat required to initiate and sustain the reaction by burning with hydrogen.

Another process, called the "Hot Wall Process," in which the energy is supplied by preheating the gases and heating the reactor wall has been developed.[2,3] Complete conversion to uranium tetrafluoride was realized by contacting gaseous uranium hexafluoride with hydrogen in a heated, vertical, open-tube reactor. Gas and reactor wall temperatures of 500 to 600°F and hydrogen excess as low as 30 per cent were satisfactory. The purity and density of the solid product met metal-grade uranium tetrafluoride specifications. Some difficulty was encountered with the accumulation of fused uranium fluorides in the tower however, and it was necessary to stop and deslag the unit about every 8 to 24 hr. Production facilities using this process have been built and operated successfully by National Lead Company of Ohio and Union Carbide Nuclear Company. Slagging has not been eliminated in the equipment, but reactor clean-out is performed on a daily basis by cooling the walls slightly and by vibrating the reactor. In view of the high processing rates possible in this system, the time lost for deslagging, about 2 hr, can be tolerated.

The reaction of uranium hexafluoride with gaseous trichloroethylene was studied before the tests with hydrogen were made. Although the reduction to uranium tetrafluoride was complete, the solid product was highly contaminated with the organic by-products of the reaction and was quite low in density.

British workers have developed a successful reduction process using carbon tetrachloride as reductant.[4] For batch operation a cylindrical pressure vessel was employed into which the uranium hexafluoride and liquid carbon tetrachloride were charged at low temperature. The reactor was then heated to 200°C, the pressure rising to 350 to 400 psi due to gaseous products, chlorine and chlorofluoromethanes. The uranium tetrafluoride, removed in the form of a friable cake, required heating in a current of air at 120°C to remove chlorine and other adsorbed gases. The carbon contamination of the product was only about 250 ppm.

For continuous operation, an inclined rotary reactor of stainless steel lined with nickel was used. Uranium hexafluoride and carbon tetrachloride gases were fed into the reactor through concentric tubes. Fins were fitted on the interior of the reactor toward the exit end and the remainder of the reactor was kept free from solid build-up by a stationary scraper arm. During normal operation at 200 to 300°C, the uranium tetrafluoride produced was continuously discharged from the end of the kiln. Some experiments were done at 450°C, at which temperature the output was more than twice that at 300°C, and the reaction took place almost completely in the gaseous phase in the form of a high temperature "flame." At the higher temperature a significant reduction was obtained in the amount of uranium tetrafluoride adhering to the kiln walls. The by-product chlorofluoromethanes are of significant industrial value, and on a large scale might be worth recovering.

## *Production of Uranium Tetrafluoride*

In a moving-bed reactor, solids charged at the top flow by gravity at their normal settled bulk density through the reactor countercurrently to the rising reagent gases and are withdrawn from the bottom as product. The use of such reactors for production of uranium tetrafluoride from uranium trioxide has been evaluated on a pilot plant scale in both the United States[6] and in Canada.[7] The reactor feed is prepared by mixing uranium trioxide powder with water followed by extrusion, drying, and curing to produce hard, hydrated uranium trioxide pellets. These are fed through two reactors in series, one for reduction to uranium dioxide with hydrogen and the other for hydrofluorination. The Canadian units are 8 in. in diameter, the reductor 15 ft tall and the hydrofluorinator 23 ft tall. The U. S. reactors (at the Feed Materials Production Center, Fernald, Ohio) are about 14 in. in diameter with effective bed heights of 10 to 12 ft. The reactors were operated separately, the uranium dioxide being collected in hoppers or drums for charging to the hydrofluorination reactor. Temperatures were controlled by adjustment of the gas feed rate and by dilution and cooling of the gas by injection of diluent gas at appropriate points.

The Fernald pilot plant installation was unable to produce specification grade uranium tetrafluoride but it did provide a basis for identification of basic design and operating parameters. Early tests showed that the hydrofluorination reactor was too short to provide the gas-solid contact, mass transfer, heat transfer and reactor control necessary to achieve a high conversion to uranium tetrafluoride. The use of two passes through the hydrofluorinator met with limited success. The pilot plant data were used to establish the conceptual design for a 5000-ton per year plant.

At the Y-12 Plant at Oak Ridge the processing of enriched uranium has, in the past, been carried out manually in small batches in order to provide for inventory control and nuclear safety. To permit an expansion of capacity, the use of a single batch-operated fluid-bed contactor for conversion of uranium trioxide to uranium tetrafluoride has been investigated.[8] Experimental operation of a pilot plant proved completely successful with a 5-in.-diameter unit, the largest permissible for nuclear safety.

The bed depth in a fluidized bed of conventional design was found to be limited to about four diameters thus limiting the processing capacity. The use of a tapered column was demonstrated with bed depths up to 14 diameters. The fluidization was found to be more stable than in conventional beds of four diameters depth. Visual observations of fluidization of uranium trioxide in a glass unit 72 in. long and with diameters of 5 in. at the base and 6 in. at the top disclosed that gas bubbles were absent and bed expansion was only 10 per cent of the expansion in a cylindrical unit.

For reactors of such small diameter the rate limiting factor in the conversion of uranium trioxide to uranium tetrafluoride was the rate at which the reagent gases (hydrogen and hydrogen fluoride) could be fed into the reactor, unless particles of large size were used to permit high gas velocities. For 20- to 40-mesh uranium trioxide produced in the Hanford continuous calciners, an average conversion to uranium tetrafluoride of 98.8 per cent was obtained in a 1-hr reduction cycle and a 1-hr hydrofluorination cycle.

## *Production of Uranic Fluoride Salts*

Alkali metal and ammonium uranium(IV) double fluorides of the general formula $MUF_5$ may be used in place of uranium tetrafluoride as intermediates in the production of uranium metal and uranium hexafluoride. An electrodialytic process for the preparation of such uranic fluoride salts from aqueous uranyl nitrate has been studied at Hanford.[9] Two electrochemical steps are performed simultaneously in the process; uranyl and nitrate ions of the feed solution are separated from each other, and uranyl ions are reduced at a mercury cathode to the tetravalent state.

The basic element of the process is an electrolytic cell divided into three compartments by anion and cation permeable membranes. When a potential is applied uranyl ions are transported from the center (feed) compartment through the cation membrane into the cathode chamber which contains ammonium (or the appropriate alkali metal) ion and fluoride ion. Simultaneously, nitrate ion migrates

through the anion membrane into the anode chamber. In the cathode chamber U(VI) is reduced to the tetravalent state and precipitated as a uranic double fluoride. In continuous operation solid is removed from the catholyte external to the cell. Greater emphasis has been placed on production of the ammonium salt since it can be readily decomposed to uranium tetrafluoride and ultimately converted to either metal or uranium hexafluoride.

Attainment of uniform membrane current density requires a parallel arrangement of membranes and electrodes. The electrolysis was studied in a laboratory cell in which the cathode was constructed as a series of stacked trenches, parallel to, and equidistant from the cation membrane. Development studies have demonstrated the feasibility of the process and indicate that it is economically competitive in certain applications. Process steps associated with product recovery and external catholyte treatment have not yet been studied in detail.

## *Preparation of Thorium Metal*

Development of a process for production of thorium metal by continuous reduction of thorium tetrachloride with sodium amalgam[10] has continued at Oak Ridge on a scale up to 3.5 lb per hour. A comprehensive summary of the development work has been recently published.[11] A total of 226 lb of thorium metal as $ThHg_3$ was produced in seven runs during 90 hr of operation. The over-all reduction yield was 82.5 per cent. Sodium excesses as low as 23 per cent were used. The product was a quasi-amalgam of $ThHg_3$ suspended in mercury, about 1 per cent thorium. Most of the mercury was eliminated by filtration to give a solid cake of about 10 per cent thorium. The remainder of the mercury was removed in a vacuum retort at 1100°C. Forty-two pounds of metal were thus isolated, having 65 to 85 per cent of theoretical thorium density and oxide contents ranging from 0.38 to 1.80 per cent (specification for reactor grade is 1 per cent oxide). Estimates indicate that the process may be operated at a cost of about $2.00 per pound including amortization of capital equipment but excluding the value of the thorium nitrate raw material.

A process for production of thorium metal by fused-salt electrolysis of thorium tetrachloride has been studied in Great Britain.[12] To avoid the difficult handling problems of the hygroscopic thorium chloride, this compound is prepared and handled as a solution in a nonreactive melt of sodium and potassium chlorides. Electrodeposition of thorium from the melt is then relatively simple. The preparation of the melt for electrolysis involves chlorination of thorium oxide suspended in a sodium chloride-potassium chloride melt. The melt is contained in a silica pot and the chlorine is fed in through a silica tube and a carbon block distributor. Iron is used as a catalyst. At 800°C chlorine reacts with the thoria in the presence of the block of carbon, the latter being slowly consumed in the process. The final melt normally contains about 40 per cent thorium and 1.5 per cent iron. The thorium is electrodeposited at a melt temperature of 700°C in a silica pot with graphite anode and molybdenum cathode. The thorium deposit is generally nonadherent to the cathode and most of it falls onto a catch plate. The metal deposit is broken free from the cathode and catch plate, crushed into small pieces and leached with water to remove the entrapped salts. The resulting metal is of high purity except for chlorine content of 400 to 600 ppm. The chlorine can be completely removed, however, by arc-melting. All stages of the process have been studied in detail on a pilot plant scale, and the results obtained suggest that the process offers promise economically.

## *Uranium Recovery from Reduction-bomb Slag*

In the production of uranium metal by reaction of magnesium with uranium tetrafluoride, a refractory material is used as a liner to protect the steel bomb shell and to prevent contamination of the uranium. A portion of the magnesium fluoride produced in the bomb as the by-product slag is ground and reused as the refractory liner material. Separation of the uranium metal and slag is not complete, and quantities of uranium, ranging from 1 to 5 per cent, are trapped in the slag as it solidifies. Development of an economical process to recover the uranium in the slag has been carried out on a pilot plant scale at Mallinckrodt Chemical Works.[13]

The process consists in grinding, screening, fluorinating with fluorine gas at 450°C in a

stirred reactor and collecting the product uranium hexafluoride. The pilot plant equipment consists of an 8-in.-diameter electrically heated Inconel tube reactor containing a 10-ft-long ribbon type screw. Slag and fluorine gas are fed into the reactor from opposite ends.

The pilot plant studies indicate that a full-scale fluorination process for recovery of uranium from slag is technically feasible. Two possible process routes were studied: (1) direct fluorination of slag, and (2) pretreatment of the slag by roasting, reduction with hydrogen, and hydrofluorination prior to fluorination. Residual uranium contents were in the range 0.14 to 0.20 per cent under the following conditions: feed rate, 100 lb per hour; slag retention time, 1 hr; fluorine use, 14 times theoretical; and temperature, 435 to 545°C.

These results are confirmed by studies at the Oak Ridge Gaseous Diffusion Plant[14] in which direct fluorination in a fluidized-bed reactor reduced the uranium content of slag from 1.7 per cent to 0.22 per cent in 5-hr residence time.

Economic analyses of the two process routes have been made and compared with costs for a phosphate precipitation process similar to the one now in use at the Feed Materials Production Center, Fernald, Ohio. Based on a fluorine cost of 50 cents per pound, the direct fluorination process is competitive with phosphate precipitation in both capital and operating costs. The pretreatment and fluorination route, particularly if integrated into existing processing facilities, would probably have an economic advantage over both direct fluorination and phosphate precipitation.

## *Processing Plants for Uranium and Plutonium*

A new uranium feed materials plant recently put into operation by Mallinckrodt Chemical Works at Weldon Springs, Missouri, has been described by Thayer.[15] This plant takes advantage of the latest improvements in technology both in refining and in metal production and fabrication. Improved operation of the solvent-extraction refining process is achieved by the use of (1) *n*-hexane as the diluent for tributyl phosphate, (2) a new type extraction equipment, called "pumper-decanters," (3) a "high" uranium concentration in the process solutions, and (4) "high" capacity pulse columns for reextraction. Improvements in uranium tetrafluoride production are achieved by (1) evaporation of uranyl nitrate solution to a composition between tri- and tetrahydrate before denitration in stainless-steel pots, and (2) the use of fluidized-bed reactors for reduction of uranium trioxide to uranium dioxide prior to hydrofluorination in "stirred-bed" reactors. In the metal production operations, the direct use of as-reduced metal ("dingots") without vacuum recasting gives a better product at lower cost. The machined dingot weighs approximately 2700 lb (about 82 per cent over-all yield from uranium tetrafluoride) and measures about 17 in. in length by 17.5 in. in diameter. This is extruded in the gamma phase to 7 in. in diameter before final forming into slugs.

The manufacturing processes and plant facilities for production of uranium hexafluoride from purified uranium trioxide at the Paducah, Kentucky, plant operated by Union Carbide Nuclear Company have been described by Powell.[16] The techniques involved are: fluidized-bed reduction of uranium trioxide, ribbon screw hydrofluorination, flame reactor conversion of uranium tetrafluoride to uranium hexafluoride, and product uranium hexafluoride condensation. Excess fluorine is recovered by reaction with uranium tetrafluoride in a separate clean-up reactor. The chemical efficiencies (fluorine and hydrogen fluoride) are high, 99 per cent, and the uranium yield is above 99.99 per cent. The continuous process yields a 99.99 per cent pure product. The plant is compact and requires few men to operate the equipment. Corrosion rates of plant equipment are low, and although nickel alloys are required in many parts of the system, extensive use is made of mild steel to reduce investment.

Elemental plutonium for use in metallurgical and pyrometallurgical research, fuel alloy development, and critical measurements is prepared at the Los Alamos Scientific Laboratory in remotely controlled equipment.[17] This equipment was designed and built at the Laboratory in 1950 to 1951. The design philosophy of the production line was to (1) contain the contamination in as small a volume as practical, (2) locate as much of the actuating mechanisms outside of the enclosure as possible, (3) construct all contaminated mechanisms as integral parts so that replacement can be made easily and without spread of contamination, and (4)

eliminate manual processing operations through rubber gloves. The process flow sheet includes peroxide precipitation of plutonium from the nitrate feed solution, filtration, washing, and drying of the precipitate, hydrofluorination, and reduction with calcium to metal. The process equipment includes various devices for remotely handling, transferring, and processing both liquids and solids inside of hood enclosures.

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